

Maximizing Wastewater Reduction for the Process Industries



Maximizing Wastewater Reduction for the Process Industries

TR-114205

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REPORT SUMMARY

This study provides an overview of water and wastewater management practices in the U.S. process industries. The focus is on the chemical and petroleum industries. It covers end-of-pipe treatment, as well as water reduction and zero discharge, since these practices evolved from end-of-pipe practices. The resulting report is a comprehensive reference developed to help utilities and energy service providers understand and focus their efforts on good business opportunities in this energy-intensive business segment.

Background

Water intake by U.S. industry is over 102 billion liters (27 billion gallons) per day. Industrial and commercial facilities discharge over 68 billion liters (18 billion gallons) of wastewater daily to surface waters or sewage systems. According to the U.S. Bureau of Census, capital expenditures by the manufacturing facilities for pollution abatement exceeds \$7 billion annually. Of this total, over \$3 billion or over 42 percent, is spent on pollution abatement of wastewater and waste solids. Operating costs related to pollution abatement exceed \$17 billion annually. Nearly 15 percent of this amount, over \$2.5 billion, is spent for fuel and electricity purchases.

Objectives

- Provide a comprehensive reference which identifies and characterizes current and potential future water and wastewater management technologies in the process industries
- Scope out opportunities for business development for utilities and energy-service providers

Approach

The project team accessed published information, utilized in-house information and expertise, and telephoned contacts. They had knowledge of the process industries, wastewater problems, and current and emerging solutions. This knowledge allowed the project team to identify existing and emerging technology growth areas and generic and specific business opportunities.

Results

The nature of this part of the process industries, important issues, what drives utility customers in this area, utility customer logic, and a number of near-term and longer term opportunities were identified.

The chemical industry is very cyclical due to periodically over building capacity, the petroleum refining industry profit margins are very stable (but only about \$0.5/BBL for many years, due to competition and environmental compliance costs), and the oil production industry is cyclical due to periodic over production on a worldwide basis. Capital and manpower is very short in these industries.

Some key water issues are the increasing cost of intake water and end-of-pipe treatment. This has been temporarily held in check by increased recycle, and using easy solutions, such as air cooling whenever economically feasible. That has resulted in high salt content streams, and only more difficult problems being left to be solved. Therefore, industries which have traditionally favored non-electric solutions may now be more receptive to electrotechnologies. This suggests the following opportunities:

- Perform Water Pinch studies which will not only assist your customers but will promote electrotechnologies
- Educate your customers through publications and workshops, using these occasions to uncover opportunities for water pinch, demonstration projects, and business opportunities
- Operate water management facilities as a business profit center

The following existing and emerging technologies look promising and should be considered for support:

- Vapor Electric Compression Evaporation—a major key for achieving zero discharge
- Freeze Concentration—a niche market fit for hazardous wastewater
- Direct Osmosis Concentration—for smaller scale niche markets such as bio-sludge dewatering, due to its tolerance for high solids loads
- Reverse Osmosis and Electrodialysis combination—to compete with thermal evaporation plus crystallization
- Electrolytic Partial or Complete Oxidation of organics—a versatile problem solver
- Microfiltration and Ultrafiltration—for various pretreatment and post treatment steps
- Advanced Distillation—has the potential to reduce U.S. evaporation losses from cooling water towers by 0.5×10^{12} lb/yr (0.2×10^{12} kg/yr)

EPRI Perspective

Chemicals, Petroleum, and Natural Gas Center target members are interested in new business opportunities for strategic load grow and load retention. Water and wastewater management concerns are wide-spread and important to their customers in the process industries. This project resulted in a comprehensive analysis and reference that provides utilities and energy service providers with information to help them focus their efforts on good business opportunities and technologies in this complex, competitive, energy-intensive, and until recently non-revenue generating, regulatory-driven part of the process industries.

Key Words

Water pinch

Water and wastewater management

Source reduction

Waste minimization

Recycle

Zero discharge

EXECUTIVE SUMMARY

The purpose of this study is to help utilities and energy service providers understand and find opportunities in the water and wastewater management area, which is pervasive throughout the industrial sector of the United States economy. There are many commonalities between various industry segments, especially in the process industries (chemicals, petroleum, pulp and paper, food, textiles, etc.). However, there are also things (technical and regulatory) that are specific to individual industries that need special handling (petroleum refining desalter emulsion problems, pulp & paper black liquor and bio-fouling, textile dyes recovery/destruction, differing regulations including different mandated control technologies, etc.). This report focuses on the chemicals and petroleum industries, and concentrates on the issues and logic of water and wastewater minimization (without and with zero discharge being the final objective), what technologies industries tend to use in this very important area and why, what new and emerging technologies are likely to make it in this very complex, competitive area, and how utilities and energy service providers can capitalize on these trends.

Twenty nine issues we identified. The top ten are summarized below, with some opportunities they suggest.

**Top 10 U.S. Chemical and Petroleum Industry
Water and Wastewater Issues**

Issues	Potential Opportunities
End-of-pipe treatment and intake water costs increasing	Water Pinch, Manage Industrial Water Operations
High salt content (recycle causing problems or at regulatory limit)	RO, RO + Electrodialysis, Vapor Compression Evaporation
Easy economic water use reduction (air cooling, etc.) already done in most existing plants	Water Pinch, Electrotechnologies' Unique Capabilities
Wastewater segregation and "at source treatment" capital cost and/or plot space limited at many existing plants	New Cost Effective, Sophisticated Separation Technologies, Electrotechnology Small Footprint
Biosludge volume reduction, dewatering and disposal	Direct Osmosis, Freeze Thaw, Manage Industrial Sludge Operations
High treatment cost hazardous wastewater	Electrolytic Partial Oxidation, Freeze Concentration + Incineration, Direct Osmosis + Supercritical Water Oxidation (for small-scale operations)
Onerous RCRA status	Same as Above, Other Electrotechnologies
Deep welling	Same as Above
Difficult streams (organic/inorganic)	Stream Specific Electrotechnologies, Electrolytic Oxidation
Desalter upsets	Microwave Emulsion Breaking, Manage Desalter Industrial Operations

Some of the key issues suggest specific electrotechnologies and/or specific potential businesses. Others suggest the opportunity to explore for electrotechnology opportunities. Utility customers are more accustomed to using traditional non-electric solutions for their normal water treatment situations. Only, when they "get in trouble on something", do they tend to start looking at electrotechnologies for a solution. As they move more towards water reuse and zero discharge, they start to look towards electrotechnologies, for their solutions to these more difficult problems. Also, for difficult end-of-pipe treatment problems, such as certain mixed organic/inorganic contaminated wastewaters, and certain high cost hazardous waste problems, they tend to venture more into the electrotechnology area.

Utility customers are also economically driven. They tend to look first at low cost non-electric solutions, and then progress towards higher cost non-electric solutions, and appear to only consider electrotechnologies when they have a very difficult problem that may not be solved in another way, or are faced with very high cost, last resort, non-electric technologies, such as incineration.

Common water/wastewater management situations—traditional technologies used and potential competitive electrotechnology solutions—are summarized below, starting with the most widely used traditional technology (biotreatment—usually lowest cost), and progressing towards the least used traditional technology (incineration—highest cost). Where available, the electrotechnology kWh/1000 gallons (kWh/m³) of wastewater processed is shown in the last column.

Competing Traditional vs. Electric Technology

Situation	Traditional	Electrotechnology	KWh/1000 Gal. (kWh/m ³)
Typical Biotreatable	Biotreatment (BT)	Currently None	
Can Precipitate	Chemical Coagulation	ElectroCoagulation	Very Low
		Electrolytic (Heavy Metals)	0.5 to >2 (0.1 to >0.5)
Biosludge Dewatering	Belt Filter Press	Direct Osmosis	340 (90)
	Centrifuge	Centrifuge	
	Drying Lagoon	Freeze Thaw	
Non-Biotreatable Organics	Wet Air Oxidation (WAO)/ BT	Electrolytic Partial Oxidation (EPO)/BT	>8 (>2)
Deep Wellable	Deep Well	(EPO)/BT	>8 (>2)
		Freeze Concentration/ Incineration (FCI)	300 (79)
Difficult Organic/ Inorganic Mixtures	Chemical Oxidation or Reduction	Stream Specific Electrotechnologies	
		EPO or Electrolytic Complete Oxidation (ECO)	>8 to >>8 (>2 to >>72)
Reclaim/Reduce Volume	Thermal Evaporation (TE)	Reverse Osmosis (RO)	20 to 30 (5 to 8)
	Extraction		
	TE/Crystallization	RO/Electrodialysis	35 to 55 (9 to 15)
	Vapor Compression Evaporation for Zero Discharge	Vapor Compression Evaporation for Zero Discharge	480 (127)
Must Destroy	Incineration	FCI	300 (79)
		Plasma	With HC liq/solid
	Wet Air Oxidation	Super Critical Water Oxidation	

There is a major trend towards recycle, reclamation, volume reduction, and handling the more difficult problems. This trend should lead to the use of more sophisticated separation and destruction processes, which provide an opportunity for electrotechnologies such as those listed above. There will also be other non-electric opportunities, such as advanced distillation (U.S. potential to reduce distillation reboiler duties by about 0.5×10^{15} BTU (5.3×10^{17} J) and condenser cooling water duties by almost as much with potential reduction in evaporative losses of 0.5×10^{12} pounds per year (2.3×10^{11} kg/yr)).

The previous suggests a number of opportunities for utilities and energy service providers. The key generic opportunities are listed below.

1. Water Pinch represents a key way of both helping utility customers, and increasing the use of electrotechnologies. It is clear from published water management treatment technology selection logic that there is a bias towards traditional non-electric approaches. The beauty of water pinch is that it not only provides plant access to utility companies, it levels the playing field, since all viable technologies are usually examined in this approach.
2. Educating utility customers relative to the benefits of some specific electrotechnologies, through publications (such as this one) and workshops should remove some of the bias, as well as uncover specific situations where utilities can be of assistance to their customers through water pinch studies, technology demonstrations at utility customer facilities, and as a provider of business services in addition to being the electric power provider.
3. For those that are interested, there is an opportunity to take over the operation of facilities' water management as a business by itself, or in conjunction with operating all utility services.
4. The existing and emerging technologies described in the table above look promising and should be considered for support (demo or other) to accelerate the introduction and implementation of these technologies throughout the industry.
5. Seven specific slipstream test opportunities were identified, where utility companies could get started.

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INTRODUCTION

This introduction covers the modern concepts that emerged from an end-of-pipe environment and mindset:

- Zero discharge
- Source reduction
- Wastewater minimization
- Internal and external recycle
- Wastewater segregation
- At-source treatment

When a novice first looks at water management practices, the subject (and even more so, the responsibility for getting something done) can be overwhelming. There are many factors that contribute to this area such as:

- A multitude of different unit operations and processes
- Conflicting vendor claims
- Different ideas on how screening and final selections should be done
- An array of sometimes conflicting water, air, and solid waste regulations (federal, state, and local)
- Conflicts between doing what is socially responsible (waste minimization, and when reasonable, zero discharge) with regulations and what is cost-effective

This report seeks to explain things in an easily understood manner. The presentation of some concepts may be over-simplified to promote understanding, with any complicating factors then further explained in detail.

1.1 U.S. Industrial Water and Wastewater Issues

U.S. industrial issues are summarized in Table 1-1, and explained in the following text.

Table 1-1
U.S. Industrial Water and Wastewater Issues

Issues	Potential Solutions
End-of-pipe treatment and intake water costs increasing	Source reduction, recycle, and rain-water capture
Source reduction introduction rate constrained by existing infrastructure and cuts in R&D budgets	Recycle and rain-water capture
Easy economic water-use reduction (air cooling, etc.) already in place at most existing plants	Recycle and rain-water capture
Recycling hitting concentration limits in existing plants	Remove salts or go to zero discharge
Wastewater segregation and “at source treatment” capital cost and/or plot space limited at many existing plants	New cost-effective, sophisticated separation technologies
Concentration based regulations limiting water recovery	Remove salts, etc. or change to mass-flow rate regulations
Command and control regulations limiting source reduction	Change to objective driven regulations
Loss of water rights in some water short areas	Grandfather water rights based on past usage

The total water intake by U.S. industries is over 102 billion liters (27 billion gallons) per day. Industrial and commercial facilities discharge over 68 billion liters (18 billion gallons) of wastewater daily to surface waters or sewage systems. According to the U.S. Bureau of Census, capital expenditures by the manufacturing facilities for pollution abatement exceeds \$7 billion annually. Of this total, over \$3 billion or over 42 percent, is spent on pollution abatement of wastewater and waste solids. Operating costs related to pollution abatement exceed \$17 billion annually. Nearly 15 percent of this amount, over \$2.5 billion, is spent for fuel and electricity purchases. These costs can only increase due to ever more stringent environmental regulations, public pressures, and growing liability issues. Pursuing better methods (source reduction and recycle, rather than just end-of-pipe treatment) can help keep costs down.

Source reduction (not making it in the first place or separating it out as it is being made) and internal (within the process) and external (outside the process) recycle are improved methods recognized by the EPA and industry. Strides have been made in source reduction, but the process still has a long way to go. This process would benefit from a long-term investment in R&D.

However, many R&D budgets have recently been cut. Also, changing the process means either scraping equipment that is still generating a profit, or waiting until the next capacity increase is needed. The latter is difficult in a time when many favor increasing capacity by de-bottlenecking existing plants, rather than building new ones. More extensive and faster results have been achieved by recycle (especially external recycle), where what would have been wastewater becomes useable water.

The amount of recycle and its rate of growth have been amazing. The ratio of the U.S. gross water use to water intake exceeds 7.5 in petroleum refining, 3 in chemicals production, 2.5 in petroleum production, and 3.5 in all manufacturing. To put things in perspective, the gross water is the amount of water that would have to be used if there was no recycle. Therefore, in petroleum refining, water intake would be in excess of 7.5 times what it is, if straight through water flow were used, without recycle.

The average annual growth rate of the gross water use to water intake ratio for petroleum refining, chemicals, and all manufacturing has been almost 10 percent per year. Even more astonishing is that this growth in recycle was accomplished while the intake water for all manufacturing was declining by more than 2 percent per year and production was growing by 3 to 5 percent per year. Reduction of intake water was primarily attributed to converting from water to air cooling for distillation column condensers, whenever technically and economically feasible. In the future, this trend will be limited to new construction, since most of the conversions to air cooling in old plants have already been made.

There are other emerging limitations. For example, a large portion of the reduction of water intake also comes from recycle, resulting in the build up of concentrations to steady state that can cause problems (product quality impairment, deposition, scaling, corrosion, plugging, increased inspection and maintenance requirements, etc.). This is a site specific situation, since the many processes in a complex can be different, the way they are tied together can be different, and the intake water quality can be different.

In the old days, “when dilution was the solution,” not much thought was given to segregating different types of wastewater (process, storm, organic contaminated, inorganic contamination, etc.). Everything (except things toxic enough to kill the biotreatment system) was treated the same way. Now, it is standard design practice to look at

1. Segregating similar wastewater streams
2. At source treatment
3. Cascading the use of poorer and poorer water
4. Minimum treatment to allow recycle of water streams to minimize overall water management costs in new plant design

However, for older plants, segregation and at source treatment can be capital cost and/or plot space prohibitive, limiting the application of these concepts.

In addition to technical barriers, there are regulatory barriers to water conservation and zero discharge. The National Pollutant Discharge Elimination System (NPDES) discharge limits are currently written with concentration limits. Also, the limits for accepting industrial wastewater by local publicly owned treatment works (POTWs) are in terms of concentrations. This has resulted in situations where water conservation measures have been taken in the absence of a water balance (not uncommon) or without examining the likely increase in concentrations relative to site permits, causing costly non-compliance. Unless regulations are designed on a mass discharge basis (with appropriate safe guards to protect aquatic and human life at and near wastewater outfalls and to protect POTW equipment), industry is faced with few good choices. They could discontinue water conservation at a site when its compliance limits are reached, consider removal of salts/other components that have built up in their system (which can be costly), or make one bold move (as opposed to the typical incremental approach) to zero discharge (where water regulations would no longer be a concern, but hazardous solid waste Resource Conservation and Recovery Act (RCRA) concerns could come into play).

The EPA (as well as industry) still has a residual end-of-pipe mindset. For example, regulations still mandate the use of specific treatment technologies (which can be different for different industries and processes). Mandated approaches are the antithesis of source reduction, which should rely on individual ingenuity to solve problems at the source. Unfortunately, industry is required to work under command and control laws, with a little deference given to those that do well at source reduction. The alternative is laws based on objectives, what is desired, and letting the companies decide how to get there.

In addition, in water short regions, regulations are written in such a way that if an individual company doesn't use its water rights, it may lose water credits potentially needed for future expansions. These regulations are currently applicable in a limited number of places in the U.S. However, water tables have been falling worldwide. This decline is a threat to agricultural production and could become an important barrier for industries in the future.

1.2 U.S. Chemical Industry Water and Wastewater Issues

U.S. chemical industry issues are summarized in Table 1-2, and explained in the following text.

Table 1-2
U.S. Chemical Industry Water and Wastewater Issues

Issues	Potential Solutions
All of the issues of Table 1-1	The potential solutions of Table 1-1
Public relations and liability	Proactive rather than reactive measures
Deep welling	Other existing and emerging methods
Onerous RCRA status	Process all hazardous wastes on site
On-site remediation	Process all hazardous wastes on site
Intangibles	Development of sustainability metrics
Inherent instability of biotreatment	Better measurement/control/designs
Improved Biotreatment	Better measurement/control/designs
Transients and random toxicity	Large up-front surge volume, better measurement/control/designs
Biosludge volume reduction, dewatering and disposal	Type of biotreatment, dewatering, and disposal technology used
Wastewater volume reduction	The subject of this report
Zero discharge	Part of the subject of this report
High treatment cost for hazardous wastewater	Part of the subject of this report (partial conversion or concentration)
Difficult streams (organic/inorganic)	Stream specific treatment
High-salt-content streams	Salt removal (RO, RO + Electrodialysis, Vapor Compression Evaporation)
Scaling, corrosion, organic film, biofouling	Removal or chemical treatment
High purity pharmaceutical or specialty chemical feed water	Appropriate technologies See TR-110887

The U.S. chemical industry produces a wide variety of products and pollutants. Some of these pollutants are highly toxic. For example, some pharmaceutical wastes are toxic down to the parts

per trillion (ppt) level. In addition, pesticide wastes are highly toxic. In fact, the beginnings of the environmental movement can be traced back to the U.S. chemical industry and situations like Love Canal, where mixed wastes were dumped in a landfill since no one knew what to do with these materials. Thus, began the Superfund era. The chemical industry took another large public relations hit when the EPA released Toxic Release Inventory (TRI) data that showed the chemical industry with the largest tonnage and variety of TRI wastes. This resulted in the chemical industry acting to protect itself both for PR and liability reasons.

However, the industry is highly motivated by economics and will usually take advantage of whatever the law allows. As a result, TRI data recently released for the chemical industry by the EPA shows that more than half the aqueous TRI wastes are still being deep welled. Deep welling is the practice of pumping wastes into a hole in the ground. The hole leads to a subterranean cavern considered to be safe. The legal departments of some large chemical companies are now questioning this practice, based on potentially huge liabilities that could occur if that material worked its way up in to an aquifer. The industry is clearly looking for better waste management practices.

However, a better way may simply be an expansion of other practices, such as injection into sulfuric acid manufacturing furnaces or other hazardous waste incinerators—or any convenient low cost alternative, such as phytoremediation. Phytoremediation is a newly developing technology that uses plants such as reeds, water lilies, and trees to process the hazardous waste. The liability risk with phytoremediation is definitely less than that for deep welling, but the PR risk is still high.

When a facility ships hazardous wastes off site for processing or disposal, it becomes a RCRA site and is subject to strict record keeping and responsibility requirements, which necessitate a large staff to properly manage. Therefore, when feasible, companies will seek to process wastes on site, to avoid the tangible costs of being a RCRA site, plus the intangible costs associated with shipping hazardous material off-site.

It is clear that for this industry, a lot of intangibles need to be considered in making decisions. The industry is struggling with ways to quantify these intangibles. One way being pursued uses sustainability metrics (BTU/Ton, kWh/Ton, Tons of waste/Ton, etc.).

A large part of this industry deals with hydrocarbons and Biotreatment (when applicable) is usually the lowest cost approach. However, biological systems have an inherent stability problem. Poor conditions and/or random toxics can easily shut a system down. Once down, they are difficult to restart. Also, excess nutrients can get the microbial flora growing too fast, leading to plugging problems (which can shut the system down, depending on the type of system) or large amounts of biosludge that must be dewatered and disposed of.

There are numerous other water and wastewater management technical problems that the chemical industry faces. These are included in Table 1-2.

1.3 U.S. Petroleum Refining Industry Water and Wastewater Issues

U.S. petroleum refinery industry issues are summarized in Table 1-3, and explained in the following text.

Table 1-3
U.S. Petroleum Refinery Industry Water and Wastewater Issues

Issues	Potential Solutions
All of the issues of Table 1-2	The potential solutions of Table 1-2
Desalter upsets	More extensive analysis and specifications for crude oil feeds, third party operation and control with chemicals, move to electroseparation if not yet done, emerging technologies such as microwave emulsion breaking
Oil, grease, and grit	Existing separator types, also desalter solutions for emulsion problems

While the petroleum industry doesn't produce the highly toxic materials produced by the chemical industry, it produces its fair share of toxics such as phenols, benzene, and polynuclear aromatics. In addition, many refineries include petrochemical operations within the refinery, or adjacent to it. In these situations the petrochemical wastewater often will be treated in the same system as the refinery wastewater, and some highly toxic materials can be present. For example, a number of refineries have pesticide production operations. Therefore, refineries potentially have the same issues as chemical plants.

In addition, refineries have some issues that are specific to refineries. For example, the desalter is an oil/water separator at the inlet of the refinery that protects the downstream equipment from corrosive saltwater exposure. As such, it is an important large equipment item. Trends in the petroleum industry are making it more difficult to operate desalters. First the trend to heavier crude oils diminishes the specific gravity differential driving force for the separation and tends to stabilize emulsions. Also, there has been a trend towards giving up control of crude oil supplies to others. This trend has resulted in unknown and variable oil field chemicals reaching the desalter, which can stabilize emulsions unpredictably. Emulsions may then reach both the process system and the wastewater system. The process contamination can lead to plugged crude oil columns as well as corrosion damage, in addition to unscheduled shutdowns. Both unpredictable emulsion carry-through to the wastewater system and the unscheduled shutdowns can create havoc with refinery biotreatment systems. In addition, any wastewater recycling is likely to end up recirculating some material to the desalter, further aggravating the problem.

Currently, refineries are moving away from gravity desalters towards electrodesalters. Also, refiners are giving control of desalters to third parties on a contractual basis and proprietary chemicals are used to control emulsions and separation.

In addition, refineries have other oil/water separators and a lot of oil, grease, and grit present that needs to be removed upstream of wastewater treatment.

1.4 U.S. Oil & Gas Production Industry Water and Wastewater Issues

U.S. oil and gas production industry issues are summarized in Table 1-4, and explained in the following text.

Table 1-4
U.S. Oil & Gas Production Industry Water and Wastewater Issues

Issues	Potential Solutions
Potential lifting of oilfield exemption; resulting costly regulations	Lobbying, delaying tactics
Miniprocess facilities	Similar to that for a small refinery
Heavy oil heater treaters with potential problems similar to desalters	Same as for desalters

Prior to production, when wells are being drilled, cutting fluids are used. Wastewaters from this process are currently exempt from regulation. However, some contamination problems have received publicity, raising awareness amongst the public and the EPA. The EPA currently is trying to define oil and gas fields as facilities, a first step towards regulation. Regulations could require the costly installation of linings for large holding ponds.

Water is produced in conjunction with oil and/or gas production. The quantity of water produced increases as operations age and can reach in excess of 90% of production. By law, this water needs to be reinjected to help maintain production and to avoid land subsidence. Before it can be reinjected, this water will need processing, at a minimum to recover oil and remove silt.

Another issue is that natural gas is often produced when the objective is oil production. The composition, amount, and market conditions may justify natural gas liquids (NGL) production and/or natural gas production. This process may require carbon dioxide removal for pipeline corrosion control. If a miniprocess facility is added to the production site, it will also have water and wastewater requirements.

For heavy oil production, cogeneration facilities or steam generation facilities will be at or near the production site. They will add to the water and wastewater requirements. Also, there is a trend towards adding miniprocessing facilities at heavy oil production operations to cut oil viscosity for pipelining. This again will add to the water and wastewater requirements.

Currently, heavy oil/water heater treaters are used for oil water separation.

1.5 Background

Current practices and systems have evolved from and integrate with end-of-pipe treatment. This section describes

- Initial understanding through wastewater analysis
- What the industry is doing with its wastewater and why
- Rule-of-thumb, end-of-pipe treatment selection logic from the literature (not friendly to electrotechnologies)
- Current water use minimization and zero discharge logic (friendly to electrotechnologies).

Water Analysis Provides Good Start to Understanding

Key measured parameters provide details about a wastewater stream.

- Biochemical Oxygen Demand (BOD) measurements indicate the amount of organic matter present amenable to biotreatment.
- Total Organic Carbon (TOC) measures the amount of organic carbon.
- Chemical Oxygen Demand (COD) measures the amount of carbon that could theoretically be oxidized to carbon dioxide.

For example, a waste stream with a high TOC and a low BOD indicates an organic waste that is not amenable to biodegradation. On the other hand, a high COD and low TOC indicates that an inorganic oxidizable species is present. Inorganic COD is usually not amenable to biotreatment. However, some inorganics are amenable to biotreatment (hydrogen sulfide, ammonia, other nitrogen compounds, phosphorus) and contribute to BOD along with the organics that are amenable to biotreatment.

- Total Dissolved Solids (TDS) is a measure of dissolved inorganics.

TDS is tracked for zero discharge applications. The TDS ends up as the major component of solid waste from a zero discharge operation. This represents the key to the “end game” that modifies water reduction/treatment logic to zero discharge logic.

The logic for treatment of primarily organic contaminated and primarily inorganic contaminated streams are reasonably straightforward. However, mixed organic/inorganics are much more difficult. A high TDS and low TOC is an inorganic stream and a high TOC and low TDS is an organic stream.

- Oil & Grease (O&G) analysis results can be made up of both dissolved and free organics. Any free O&G needs to be removed prior to treatment.
- Gritty solids (not normally analyzed for, but determined by on site inspection or experience) normally should be removed up-front.
- Odor and organic-based color normally need a strong oxidant at an appropriate point in the process.

- Cyanides, toxic organics, phenol, and heavy metals all are problems for biotreatment systems and suggest special processing.

Table 1-5 below shows typical wastewater contaminants, typical effluent limitations, and typical implications.

Table 1-5
Typical Contaminants, Effluent Limitations, and Implications/Concerns

Parameter	Effluent, mg/L	Implications
TOC		<ul style="list-style-type: none"> • Measures organics • Can be toxic • Depletes O₂
TDS		<ul style="list-style-type: none"> • Measures inorganics (salts) • Can be toxic to aquatic life and agriculture
COD	300 to 2000	<ul style="list-style-type: none"> • Can be toxic • Depletes O₂
BOD	100 to 300	<ul style="list-style-type: none"> • Depletes O₂ in receiving waters
O&G	15 to 55	<ul style="list-style-type: none"> • Damages vegetation and wildlife • Remove free O&G first
TSS	15 to 45	<ul style="list-style-type: none"> • Turbidity • Toxic to aquatic life
pH	6.0 to 9.0	<ul style="list-style-type: none"> • Acidity or alkalinity is toxic to aquatic life
Temperature	< 40°C	<ul style="list-style-type: none"> • Toxic to aquatic life
Color	2 color units	<ul style="list-style-type: none"> • Aesthetic problems • Destroys algae
Odor		<ul style="list-style-type: none"> • Can be toxic to aquatic life and humans • Aesthetic problems
Redox Ptnl		<ul style="list-style-type: none"> • Can be toxic to aquatic life
NH ₃ /NO ₃	1.0 to 10	<ul style="list-style-type: none"> • Toxic to aquatic life • Eutrophication (algae)
Phosphates	0.2	<ul style="list-style-type: none"> • Eutrophication (algae)
Heavy Metals	0.1 to 5.0	<ul style="list-style-type: none"> • Toxic to aquatic life and humans
Surfactants	0.5 to 1.0 total	<ul style="list-style-type: none"> • Toxic to aquatic life and humans • Aesthetic problems
Sulfides	0.01 to 0.1	<ul style="list-style-type: none"> • Toxic to aquatic life and humans • Aesthetic problems
Phenol	0.1 to 1.0	<ul style="list-style-type: none"> • Toxic to aquatic life and humans • Aesthetic problems
Toxic Organics	1.0 total	<ul style="list-style-type: none"> • Toxic to aquatic life and humans
Cyanide	0.1	<ul style="list-style-type: none"> • Toxic to aquatic life and humans

What Industry Is Doing With Its Wastewater

For all industry wastewater

- 50% is biotreated
- 25% undergoes chemical precipitation (mostly for heavy metal removal) followed by biotreatment
- 10% is deep welled
- 6% undergoes other inorganic/organic separation
- 3% undergoes other organic
- 2% undergoes chemical precipitation
- Less than 1% is incinerated
- Remaining 3% is unidentified

Discharges for the chemical industry (producing a lot of toxic waste)

- 50% to underground injection wells (deep welling)
- More than 25% goes to surface waters
- Remaining 25% goes to off-site disposal and land releases

Why Industry Uses Current Wastewater Disposal Practices

Industry is clearly driven by economics. Biotreatment is the lowest cost approach for materials that can be reliably bio-treated. For hazardous materials that would normally require costly approaches, deep welling is the lowest first-cost approach if there is a site with appropriate subsurface conditions within a reasonable distance from the source of pollutant. On a long-term basis, the legal departments of some major companies are questioning this practice. The potential liabilities that could occur if toxic material broke up into an aquifer would more than wipe out any initial cost savings, in both lost goodwill and legal costs.

Table 1-6 lists cost information for a number of technologies that are primary treatment technologies. Note that biotreatment of less than 1000 mg/L BOD wastewater ranks lowest in cost and incineration ranks highest.

Table 1-6
Cost of Primary or Potentially Primary Treatment

	\$/Million Gallons ($3.8 \times 10^3 \text{ m}^3$)	
Bio < 1000 mg/L BOD	40 to 500	270
Carbon adsorption	70 to > 1000	> 535
Ion exchange	250 to > 1000	> 625
Bio > 5000 mg/L BOD	> 1000	> 1000
Membrane	30 to > 2000	> 1015
Precipitation	50 to > 2000	> 1025
Thermal crystallization	> 5000	> 5000
Chemical oxidation	200 to 10,000	5100
Solvent extraction	1000 to 10,000	5500
Evaporation thermal	> 10,000	> 10,000
Freeze concentration	30,000 to 40,000	35,000
Incineration	> 1,000,000	> 1,000,000

Table 1-7 lists cost information for a number of technologies that are auxiliary treatment technologies. Note that evaporation ponds rank lowest in cost and freeze concentration ranks highest.

Table 1-7
Cost of Auxiliary or Potentially Auxiliary Treatment

	\$/Million Gallons ($3.8 \times 10^3 \text{ m}^3$)	
Evaporation ponds	20	20
Filtration	20 to > 100	> 60
Flotation	20 to > 100	> 60
Stripping	40 to 250	145
Gravity separation	50 to 500	275
Solidification and stabilization (cement)	10 to 1000	505
Carbon adsorption	70 to > 1000	> 535
Ion exchange	250 to > 1000	> 625
Membrane	30 to > 2000	> 1015
Centrifugal separation	60 to > 2000	> 1030
Thermal crystallization	> 5000	> 5000
Solvent extraction	1000 to 10,000	5500
Evaporation thermal	> 10,000	> 10,000
Freeze concentration	30,000 to 40,000	35,000

Rule-of-Thumb Treatment Selection Logic

The rule-of-thumb treatment selection logic for a specific stream is illustrated by the following series of figures. There are separate figures for common pretreatment (Figure 1-1), inorganic (Figure 1-2), organic (Figure 1-3), and mixed organic/inorganic (Figure 1-4) contamination, and water use minimization (Figure 1-5). Examination of these figures suggests the types of streams that should be segregated.

Whenever mixing streams leads to more costly treatment, they should be segregated (assuming the capital and plot space is available). Streams, that if mixed with any other streams would lead to more costly treatment, should be “at source treated” (assuming the capital and plot space is

available). Therefore, the individual treatment logic also leads to the logic of stream separation and “at source treatment.”

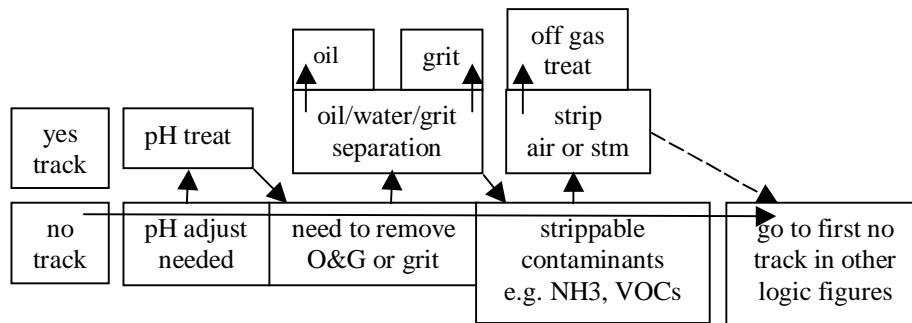


Figure 1-1
Pretreatment Logic

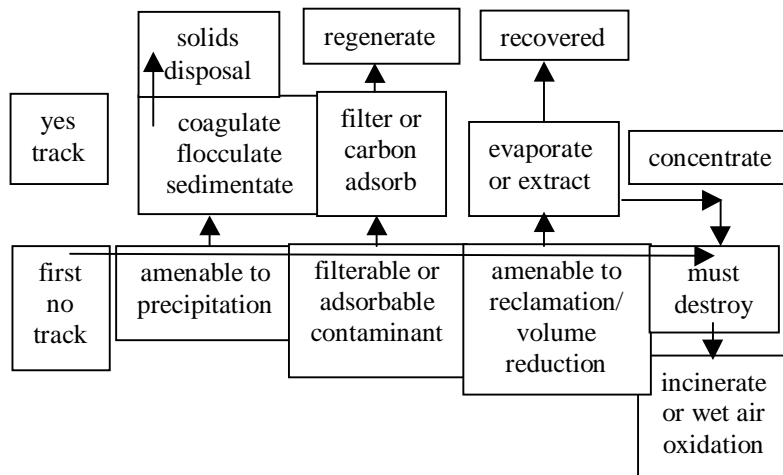


Figure 1-2
Inorganic Logic

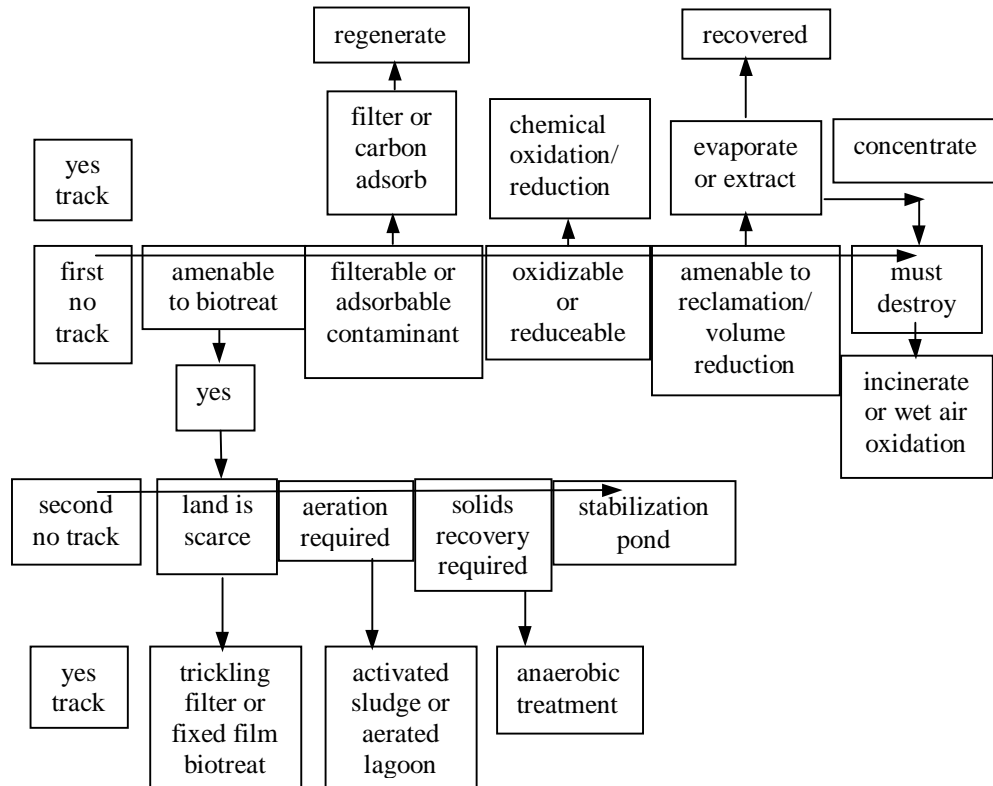


Figure 1-3
Organic Logic

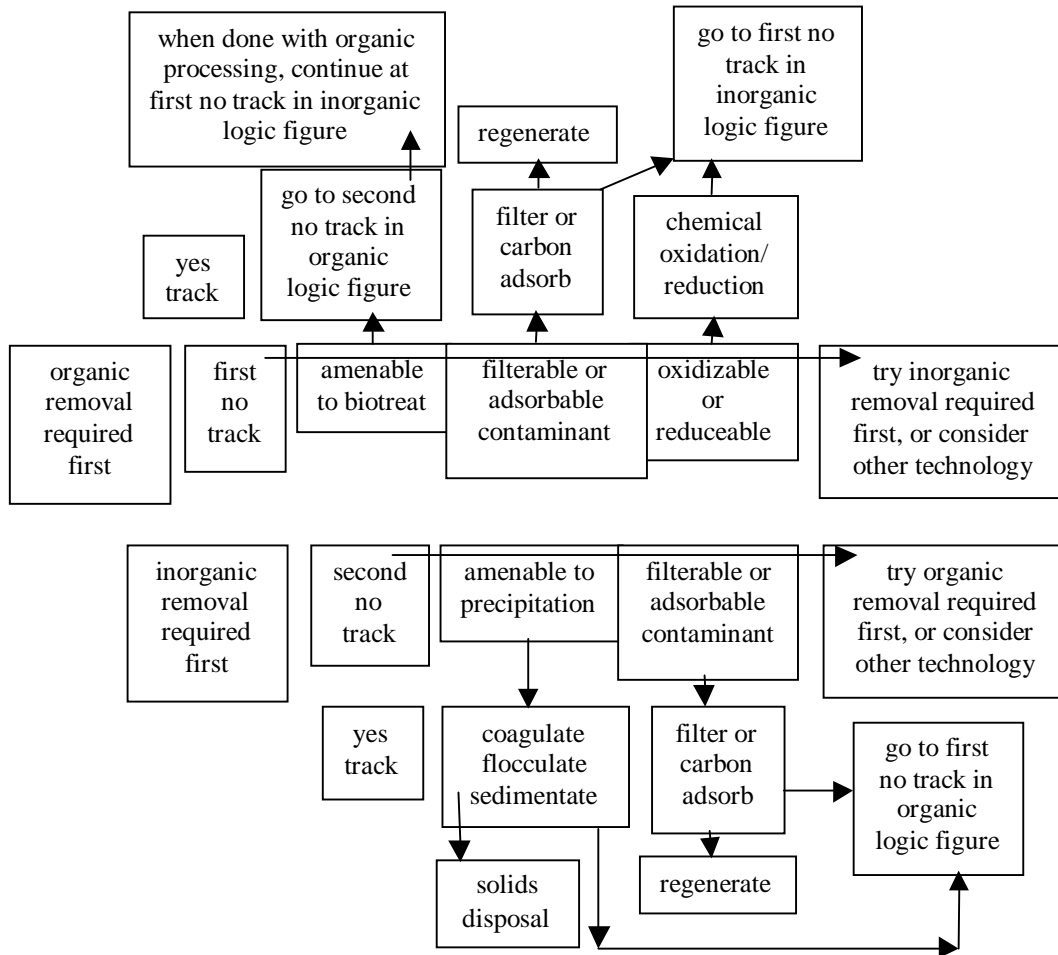


Figure 1-4
Mixed Organic/Inorganic Logic

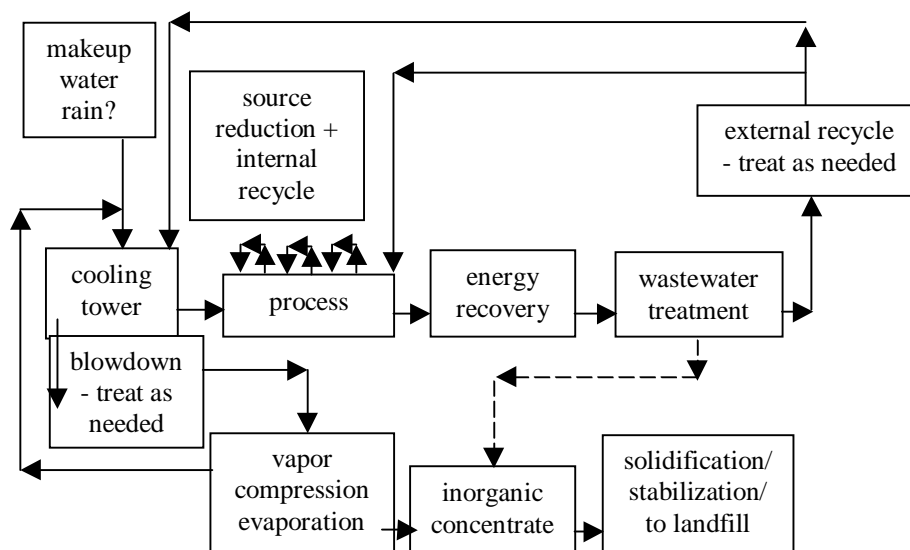


Figure 1-5
Water Use Minimization Logic

The five logic diagrams have been adapted from material in the literature. The first four come from an end-of-pipe treatment mind set. The order of the steps are based on a simplistic logic, where mitigating circumstances could dictate changes in the order of the steps. For example, in Figure 1-1, pH treatment is done first to protect downstream equipment from corrosion. If that would cause emulsification, then the oil separation step should come first. The oil, grease, and grit are removed prior to stripping to avoid fouling the column. If the wastewater is producing gas bubbles, an air flotation separator could be used instead of a gravity separator, and the air stripping would be done in that separator. The line from the air stripping box to the “go to first no track in other logic figures” box is dashed, since on occasion, no further processing may be needed.

The “no tracks” in Figure 1-2, 1-3, and 1-4 move from generally lower cost technologies towards higher cost technologies. When a “yes” answer is reached, that will remove the waste from the “no track” before getting to a higher cost technology. Also, examination of these three figures shows some specific technologies such as chemical oxidation, evaporation, and carbon adsorption. These are familiar technologies that are usually selected by the environmental community. However, there may be better existing or emerging alternatives.

Alternative Technologies

The following are examples of some alternative technologies to consider.

Electrolytic Complete or Partial Oxidation of Organics

In this emerging technology, complete electrolytic oxidation could substitute for chemical oxidation of hazardous organics in Figure 1-3 and 1-4. Partial electrolytic oxidation could move

a hazardous organic from a track towards high cost incineration to one towards low cost biotreatment.

Ozone

Ozone is a chemical oxidant recognized by the environmental community, but not widely used in the chemicals and petroleum industries.

Reverse Osmosis Plus Electrodialysis

Another possibility would be to replace the thermal evaporation referred to in these figures with reverse osmosis coupled with electrodialysis of the concentrate. This process would achieve similar extents of concentration for inorganic streams and some mixed inorganic/organic streams.

In addition, carbon adsorption (producing hazardous solid waste) can be replaced with reverse osmosis coupled with electrodialysis of the concentrate. This process produces a more manageable concentrated hazardous liquid waste for inorganic streams and some mixed inorganic/organic streams.

Freeze Concentration

Freeze concentration should be considered when hazardous VOCs rule out evaporation for concentration.

Water Use Minimization Logic

Using this logic (Figure 1-5), the first thing to consider is source reduction and internal recycle. Then, external recycle of wastewater treatment effluent and cooling tower blowdown should be considered. Finally, the capture and use of rainwater should be considered.

These practices can minimize water use. The key to zero discharge (“the end game”) is currently wastewater treatment effluent recycle to the cooling water tower and vapor compression evaporation (an electrotechnology) of the cooling tower blowdown to recycle water and produce a concentrated slurry. This slurry can be solidified and stabilized to produce a solid waste for either regular landfills or hazardous landfills.

2

TECHNOLOGIES FOR PREVENTION/REDUCTION/TREATMENT

This chapter described some key technologies for pollution prevention, reduction of wastewater, and end-of-pipe treatment.

2.1 Process Changes—Pollution Prevention by Source Reduction

The concept of source reduction is to avoid making pollutants in the first place. Fundamental changes in the reaction pathways (raw materials and chemical reactions) are at the heart of source reduction. However, advanced reactor design changes and avoidance of water use (for washing, air coolers, etc.) can also lead to source reduction.

Utility companies may have difficulty participating in source reduction activities at a customer's site. Customers often do not wish to share their proprietary processes. However, there may be opportunities to get involved through revolutionary generic reactor design changes. Also, performing a water pinch study may allow utilities to identify reactor upgrade opportunities.

2.1.1 *Advanced Reactors*

Two advanced reactor design concepts are ultra-low reactor residence times and combined reaction and separation (such as reactive distillation). These designs are aimed at improved selectivity (higher production of what is wanted and less waste production).

Low residence time avoids unwanted side reactions. Removing reaction products as the reaction proceeds can also avoid unwanted side reactions, and/or adjust concentrations (for reactions that are equilibrium controlled, rather than being reaction rate controlled). Adjusting concentrations for equilibrium controlled reactions can both increase reaction rate and improve selectivity.

Numerous designs have been reported in the literature, and there is a commitment to long-term R&D in this area. Some reactor designs are generic and will help in a wide range of reactions. Others are specific for a given reaction and set of operating conditions.

2.1.2 *Water Pinch Analysis*

While water pinch is usually conducive to finding internal and external recycle opportunities, it could lead to source reduction when water is produced or consumed in the production reactions.

As previously mentioned, performing a water pinch study may allow a utility company to view the customer's process and identify potential reactor upgrade opportunities (even when water is not involved in the chemical reactions). See the next section for more on water pinch.

2.2 Recycle and Reuse—Reduction

The largest potential for utilities to impact their customers' operations is in recycle and reuse technologies. Here again, water pinch is an excellent way for utilities to explore opportunities to better serve their customers.

2.2.1 Water Pinch Analysis

The previously shown logic diagrams and designs come out of traditional design methodology. This methodology is based on experience and trial-and-error attempts at optimization. Since there isn't enough time or money to investigate every alternative, the traditional approach usually leads to sub-optimization.

The thermal pinch approach has been highly successful, since it is based on a systematic computerized approach that sets thermodynamically achievable targets for a system and then finds economically viable approaches to move towards that target. Water pinch is an adaptation of thermal pinch to the water/wastewater system. In thermal pinch, temperature versus mass flow rate times specific heat is used to find the thermodynamic temperature pinch point. In water pinch, pollutant concentration versus aqueous-stream mass flow rate is used to find the concentration pinch point.

Water pinch is a much more complex problem, since there is usually more than one pollutant to be considered and the number of technology approaches available are great. However, water pinch studies have shown good results and they represent a way of getting electrotechnology approaches considered, since all approaches are "on-the-table," not just the ones that the environmental community favors.

2.2.2 Thermal Evaporation

Thermal evaporation (when volatiles are not present) is the workhorse of the industry. Streams are concentrated and quality distillate water is recovered.

At high levels of concentration, salt can separate out. If this occurs, it would have to be collected and disposed of, with or without leaching stabilization.

When hazardous volatiles are present, freeze concentration can be a better alternative (see the freeze concentration section).

2.2.3 Reverse Osmosis Plus Electrodialysis (35 to 55 kWh/1000 gal. (3.8 m³))

The combination of reverse osmosis (RO) and further concentration of the RO concentrate by electrodialysis should be a competitive technology to thermal evaporation. However, as can be seen by the selection logic diagrams, the process industries might not even consider this possibility. If utilities performed a water pinch study which indicated that this type of recovery and/or concentration step was warranted, industries might consider it as an alternative to thermal evaporation.

2.2.4 Vapor Compression Evaporation (An Electrotechnology for Zero Discharge—480 kWh/1000 gal. (3.8 m³))

Figure 2-1 shows the process arrangement for vapor compression evaporation. This electrotechnology is currently a key component of zero discharge systems. Vacuum conditions are required due to the high solids concentration, which makes electric drives the preferred drive for all mechanical equipment.

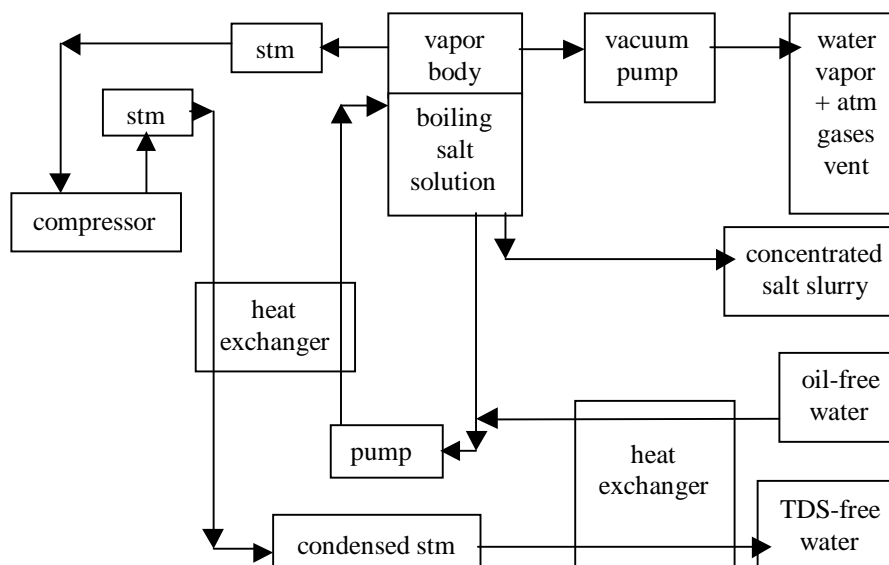


Figure 2-1
Vapor Compression Evaporation

The evaporator system purges dissolved solids (in a highly concentrated form), that would otherwise build to unacceptable concentrations, from the cooling water through evaporative cooling losses. The evaporator is a vapor compression forced circulation design. The source of heat for evaporation is the condensation of vapors drawn from the vapor body under partial vacuum (drawn by an electric motor powered compressor). The recirculation system is designed so water evaporation occurs on the water surface in the evaporator body and not at the heat exchanger interface. This design, in addition to pumping the high-suspended solids slurry that scours the heat transfer surface, prevents the accumulation of difficult-to-clean scale on the brine side of the heat transfer surfaces in the evaporator heat exchanger.

Feedwater recovery in the evaporator is greater than 99%, with only 10 mg/L dissolved solids in the distillate. The brine recovered from the evaporator contains high concentrations of trace contaminants from plant process feedwater; salt forms of ions leached from cooling water contact with any material and high concentrations of all the inorganic cooling water chemicals. The system uses 480 kWh/1000 gallons (3.8 m³) of feed.

2.2.5 Freeze Concentration of Hazardous Wastewater (300 kWh/1000 gal. (3.8 m³))

Freeze concentration upstream of incinerators has been commercialized in two overseas facilities at 2 MW and 3.5 MW levels. This technology is applicable when either incineration or supercritical water oxidation is required, and the hazardous material is a mix of non-volatile hazardous material and volatile hazardous material (hazardous VOCs). In the absence of the hazardous VOCs, thermal evaporation would be less costly. In their presence, the vapor from the evaporation step would also have to be incinerated, making freeze concentration/incineration less costly than evaporation/incineration. If only hazardous VOCs are present, the stream could be air stripped and followed by catalytic oxidation. The incinerator then wouldn't be needed. Therefore, freeze concentration has a niche market where both hazardous VOCs and hazardous non-volatile materials requiring incineration or super critical oxidation exist.

The following is a description of how freeze concentration was selected for two hazardous wastewater applications. This account is instructive and covers a wide range of considerations taken account when making these types of decisions.

Niro Process Technologies B.V. needed to help a client find a hazardous wastewater management design that would be based on proven, reliable, flexible, cost-effective, environmentally friendly, and safe technology. Biotreatment systems have been proven for many waste streams but there are also specific toxic components precludes its use, as was the case for this client. Incineration is the workhorse in the chemical industry and is capable of safely destroying a wide range of toxic components. However, it is expensive. Super critical water oxidation can destroy the organics and doesn't require a following biotreatment system. But this system is not proven above a capacity of about 1 m³/hr. At that scale, 35 parallel reactors would be needed, which is cost prohibitive. The other oxidation treatments, operating with high pressure (20 to 200 bar) (2000 to 20,000 kPa) and medium temperature range (150°C to 350°C), have also seen commercial service. Most are not capable of completely destroying the organic components, but rather reduce the organic load by 75 to 80% and modify the nature of the organics so that a biotreatment system can safely handle the waste. Each new waste needs rigorous oxidation and biotesting before it can be scaled for commercial use. Evaporation and freeze concentration (FC) are pre-treatment steps that can be used to reduce the overall costs of incineration. Evaporation is a well-developed unit operation with applications in many industries. Freeze concentration has been proven in over 50 commercial installations in the food industry.

Budget costs for the remaining viable options in dollars per cubic meter, were estimated to be \$30 to \$45 for thermal wet air oxidation (both types) and biotreatment, \$35 to \$50 for catalytic wet air oxidation and biotreatment, \$90 to \$125 for direct incineration, \$70 to \$95 for evaporation and incineration (total stream), and \$35 to \$50 for freeze concentration and

incineration. The cases including wet air oxidation do not include costs for treating off gases, which generally need further treatment.

Freeze concentration and incineration costs were projected to be similar to any of the viable oxidation steps and biotreatment. However, FC and incineration presented a positive approach because

- A bio-system didn't need to be proved out
- A holding pond or large surge vessels would have been needed (adding to costs) to even attempt to match FC's flexibility and reliability relative to anticipated changes in both feed flow rate and composition
- Biosystems are subject to shut down due to random toxics (even with large up-front surge volumes)
- FC plus incineration rated better in the areas of environmental impact and safety

The selective nature of the crystallization process used in FC and the large bulk volume of the system allow for a rather wide variation in feed composition. Water is crystallized to ice and since water is the bulk of the waste stream, the rest of the solution plays a minor role in the concentration process. The system can easily absorb normal system fluctuations.

Examination of this specific case, with high water content waste including volatile organic components, shows that FC pre-concentration can significantly reduce the impact of the incinerator on the environment. This is achieved by reduction of the feed to the incinerator and results in a reduction in fuel gas consumption (and subsequent reduction of CO₂ produced). An evaporator may also be used to concentrate the waste, but in the case of volatile organic components, the vapor will also need to be incinerated. This will not reduce the size of the incinerator although the fuel gas consumption may be reduced since a portion of the feed is already vaporized.

The traditional approach would have been incineration or evaporation and incineration. However, a common rule of thumb states not to use evaporation when VOCs are present. Wet air oxidation plus biotreatment is an alternative to consider, but the uncertainties of untried compositions of hazardous wastes tends to preclude its consideration. FC plus incineration was not a traditional approach at the time that this work was performed.

The freeze concentration process is based on a proprietary crystallization method combined with a mechanical separation technique (wash column). The crystallization takes place in surface scraped heat exchangers from which the initially small crystals are supplied to recrystallizer vessels. The crystals grow to 100% pure spherical crystals in the recrystallizers (ripening effect). The crystals are ideal for separation in the wash columns, where they are separated from the concentrated liquid by counter-current washing with byproduct water. The result of this separation process is that ultra pure water (from the melted ice crystals) is made as a byproduct, and the concentrate is separated for incineration without dilution. See Figure 2-2.

In mid-1997, the first full-scale application of FC for a hazardous wastewater application was started up in an Asian chemical plant. The plant processes nearly 200,000 MT per year of

wastewater (almost a 2 MW load). A second unit started up in September 1999, in Europe with double the capacity (3.5 MW load) of the first unit. The European complex involved the use of six recrystallization units in series (each with its associated motor driven scraped surface heat exchanger crystallizer and motor driven recrystallizer stirrer) and seven wash columns in parallel (each with two motor driven proprietary mechanisms).

The FC plus incineration hazardous water management approach reduced operating costs relative to incineration and evaporation plus incineration. However, capital costs were similar. The system is highly environmentally friendly (conserves water, uses less fuel, and insures against inadvertent releases of VOCs). The savings were \$50 to \$75 per m³ of feed relative to incineration. It also saved \$35 to \$45 per m³ of feed relative to evaporation plus incineration.

The first application for the system was a 50 MT/hour caustic wash water from styrene monomer/propylene oxide production, with 18 MT/hour byproduct water recovery containing <50 ppm total dissolved solids in the recovered water (May 1997 startup). The second system application was for 100 MT/hour caustic wash water from styrene monomer/propylene oxide production, with 34 MT/hour byproduct water recovery containing <50 ppm total dissolved solids in the recovered water (September 1999 startup).

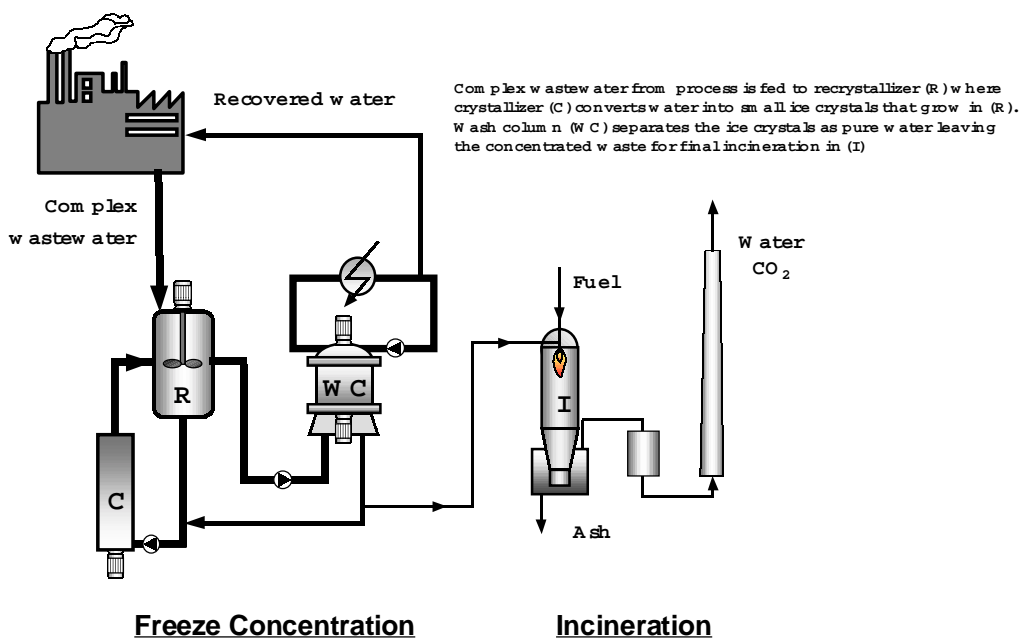


Figure 2-2
Incineration and Freeze Concentration

2.2.6 Direct Osmosis Dewatering of Bio-Sludge (340 kWh/1000 gal. (3.8 m³))

This technology (see Figure 2-3) uses a combination of reverse osmosis (RO) and direct osmosis (DO) to concentrate aqueous streams. The RO loop concentrates clean (solids-free) brine (from say 5% to 9%) to provide the driving force for water transfer into the brine stream in the DO part of the system, thus concentrating the stream of interest in the DO part of the system without the

use of pressure differential as the driving force. This approach prevents membrane solids fouling (minimizing membrane cleaning, wear, maintenance, costs, and downtime, maximizing flux and resulting in good overall economics). Like freeze concentration, this technology was first applied in the food industry for applications such as concentrating tomato paste and wine. In mid-1998, it was applied in the U.S. for concentration of landfill leachate at 1.41 kg/s (5 Metric Ton/hr) (500 kW).

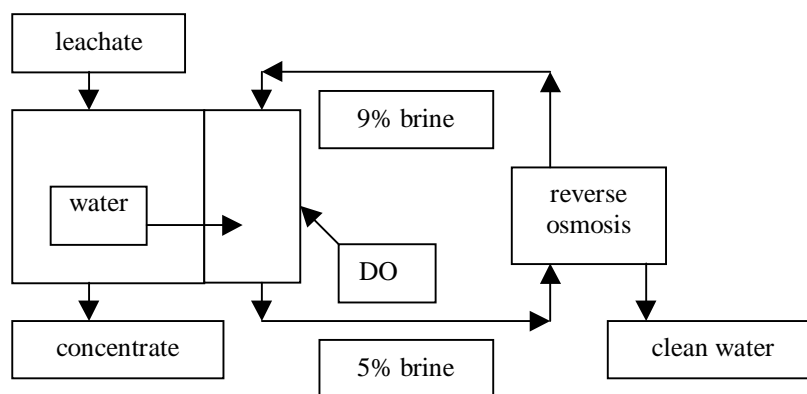


Figure 2-3
Direct Osmosis System

The DO technology may prove to be broadly applicable for bio-sludge dewatering, due to its high tolerance for solids, its previous success in concentrating tomato paste, and the broadly pervasive use of biotreatment technologies for wastewater management.

DO may compete with freeze concentration in many areas. However, each of these technologies will have unique market niches due to the characteristics of the technology. For example, freeze concentration will tend to be applied for large capacities, small molecular sized contaminants, and high salt concentrations. DO, which is modular, doesn't have the economies of scale as freeze concentration. DO will pass small molecules through the membrane, while freeze concentration is not affected by small molecular contaminants. High salt content streams will make it impractical to use RO to generate the required DO salt concentration driving force.

On the other hand, DO will tend to be applied when the application is at low capacity, low salt concentrations, low extent of water concentration, and high free solids content. DO is appropriate due to the economy of scale and salt driving force characteristics, lower specific electricity requirements at low extents of concentration (freeze concentration requires 360 MJ/Metric Ton (100 kWh/Metric Ton) of byproduct water independent of the extent of concentration, while DO's requirement decreases from 342 MJ/Metric Ton (95 kWh/Metric Ton) of byproduct water at 95% concentration to very low kWh/Metric Ton loads for low extents of concentration, such as those applied for wine concentration), and DO's capacity to handle high free solids situations without a solids separation system.

2.2.7 Electrolytic Destruction or Modification of Hydrocarbons (8.5 kWh/1000 gal. (3.8 m³) in One Modification Application)

Using this technology, pollutants have been successfully destroyed to low PPB levels (aromatics, phenols, nitroaromatics, alcohols, carboxylic acids, aliphatics, amines, halogenated compounds, microorganisms). Electricity is the only added component (no solids or odors) when this technology is applied. Costs are dependent on conductivity, type of molecule, concentration change, and extent of destruction. The technology can be applied so the pollutants reduce to CO₂ and H₂, or less toxic materials (i.e. benzene to acetic acid). The cost ranges from \$0.13 U.S. to \$0.53 U.S./m³ (\$0.5 U.S. to \$2 U.S./1000 gal (3.8 m³)) for some applications.

The technology is potentially usable upstream of evaporators and biotreaters, and for mixed organic/inorganic streams (areas where organics or toxics are a problem). Textile, food, and fine chemicals effluents have been successfully treated with this technology. There is an existing 7.9 L/s (125 U.S. gpm) pilot unit and a 0.0158 L/s (0.25 gpm) desktop demo unit. These are available for purchase or lease for proprietary self-testing (purchase for \$25,000 U.S. and \$9250 U.S., respectively, lease for \$2000 U.S./mo. and \$800 U.S./mo., respectively). The vendor plans to eventually build a mobile unit in a mini-van. Also, the vendor will test a limited number of samples free, if there is real potential for a commercial installation (based on estimated capital and operating costs). Commercial modules would be 82 to 114 L/s (1300 to 1800 U.S. gpm).

This is a versatile technology that can potentially solve a number of difficult problems. If there is a difficult organic/inorganic mixture that can't be economically handled with other approaches, just "zap" away all of the hydrocarbons or change them to something that can be handled. If there is something in a stream that makes it not amenable to biotreatment, just "zap" it to something that can be biotreated. If hydrocarbons need to be removed to protect an evaporator from heat transfer fouling or protect a membrane system from hydrocarbon induced damage, just "zap" away the hydrocarbons to the PPB level. The technology is clearly applicable for both recycle and end-of-pipe treatment.

2.2.8 Microfiltration and Ultrafiltration (4 to 8 kWh/1000 gal. (3.8 m³))

These membrane technologies can be used prior to the step to protect downstream equipment, or after as a polishing step. They are applicable in both recycle operations and end-of-pipe treatment.

2.2.9 Other Membrane Processes

Reverse osmosis, electrodialysis, microfiltration, and ultrafiltration technologies covered earlier are the membrane technologies that receive the most attention in the chemicals and petroleum industries. Table 2-1 shows the various membrane processes and the competing conventional technologies.

Table 2-1
Examples of Membrane Applications and Alternative Separation Processes

Process	Applications	Alternative Processes
Microfiltration	Separation of bacteria and cells from solutions	Sedimentation, Centrifugation
Ultrafiltration	Separation of proteins and virus, concentration of oil-in-water emulsions	Centrifugation
Nanofiltration	Separation of dye and sugar, water softening	Distillation, Evaporation
Reverse Osmosis	Desalination of sea and brackish water, process water purification	Distillation, Evaporation Dialysis
Dialysis	Purification of blood (artificial kidney)	Reverse Osmosis
Electrodialysis	Separation of electrolytes from nonelectrolytes	Crystallization, Precipitation
Pervaporation	Dehydration of ethanol and organic solvents	Distillation
Gas Permeation	Hydrogen recovery from process gas streams, dehydration and separation of air	Absorption, Adsorption, Condensation
Membrane Distillation	Water purification and desalination	Distillation

Figure 2-4 shows the filtration size spectrum and the applicable technologies. The figure extends down through the atomic radius range which is applicable for all of the technologies in Table 2-1, with the exception of micro-, nano- and ultrafiltration.

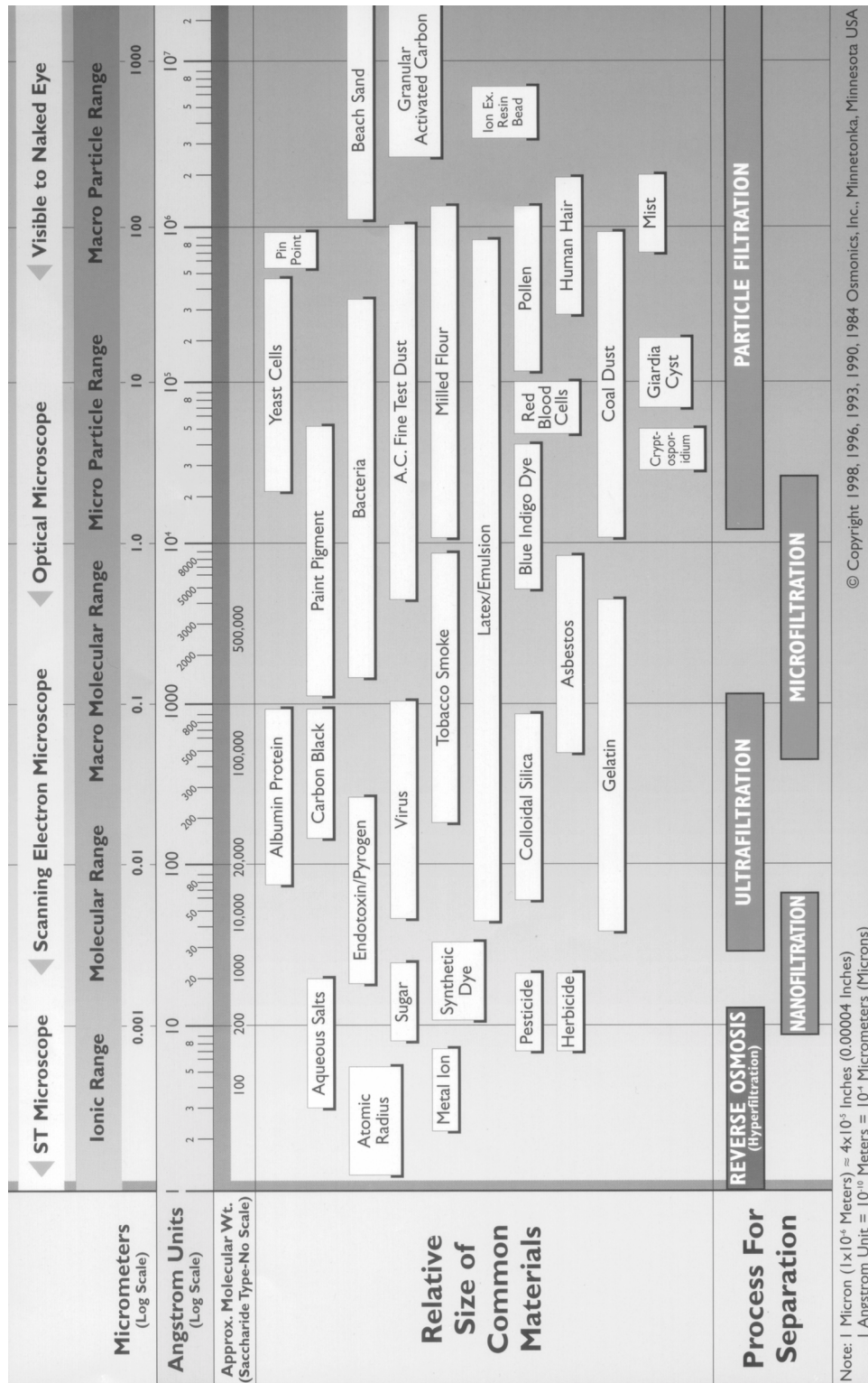


Figure 2-4
The Filtration Spectrum

2.3 End-of-Pipe Treatment Technologies

The most common end-of-pipe technologies are summarized in Figures 1-1 through 1-4. As mentioned earlier, these logic diagrams fail to recommend electrotechnologies (except possibly aerated lagoons). The technologies used in these diagrams are those most familiar and comfortable to the environmental community.

Areas for the utility provider to promote electrotechnologies are those that start to bridge the gap between end-of-pipe treatment and recycle, and those related to difficult mixed organic/inorganic streams.

For the end-of-pipe treatment and recycle areas, the combination of RO and electrodialysis can compete with thermal evaporation, and vacuum vapor compression evaporation can replace thermal evaporation when high solids contents are involved (as zero discharge is approached).

For difficult mixed organic/inorganic streams, a dead-end is reached in the logic diagram Figure 1-4. The company is “between a rock and a hard place.” If organics are the problem, electrolytic modification or destruction of the organics could be the solution. When the inorganics are the problem, various membrane processes may be the solution (using organic resistant membranes and potting materials).

Additional end-of-pipe electrotechnologies that could be considered are discussed in the next section.

2.3.1 Ozone

Ozone has been successfully used in commercial water cooling towers to replace chlorine and chemical additives (for corrosion, biofouling, scale formation, etc.).

However, it has been difficult to make similar inroads in the chemical and petroleum industry, due to different conditions. In these operations, cooling water temperatures go to over 130°F (54°C), which doesn't allow scale controlling chemicals to be removed, diminishing the benefit. Also, the residence time in the cooling water loop is usually at least 15 minutes, which is in excess of ozone decay times. An ozone system would require distributed entry ports to control biofouling, which would decrease heat transfer rates, and shorten times between required heat exchange cleanings.

Plant management has not been willing to go to such a complex system. In addition, plant management has abdicated control of their cooling systems to the chemical additive vendors by becoming dependent on their recommendations. Therefore, the outlook for ozone in this industry is not promising. There have been some inquiries relative to testing this technology in these industries, so an opportunity for utility companies may still exist.

2.3.2 Ultraviolet (UV)

Some interesting work has been done in this area, but system reliability (due to fouling of the transparent surfaces) will continue to be an issue in these industries.

2.3.3 Plasma

Plasma furnaces are a competitor to conventional incineration. The emphasis here has been on hazardous solids destruction. However, work has also been done on aqueous wastes. If aqueous wastes are commercially processed via plasma, it will probably be done in conjunction with destruction of hazardous liquid organic wastes and/or solid wastes. Under these conditions, the following practices would apply.

Best Demonstrated Available Technologies (BDAT) are hazardous landfilling and incineration. Hazardous landfilling costs in excess of \$1000/ton (exclusive of transportation, RCRA management costs, and potential intangible liability costs). Off-site incineration costs range from \$400 to \$2000/ton (exclusive of transportation, RCRA management costs, and potential intangible liability costs). Many factors are considered in arriving at the off site incineration price including heating value, acid gas neutralization, NO_x and SO_x produced, volatile heavy metal content, compatibility with other wastes (blendability), and special handling requirements.

For many hazardous wastes, EPA specifies incineration as BDAT. Plasma process are not only equivalent to incineration because of the extremely high destruction and removal efficiencies (DRE) achieved, but surpasses BDAT because they can recycle waste to commercial products, namely syngas and/or glassy product. The value of these products and the cost of landfilling waste residuals from incineration are two factors that provide process cost advantage for plasma technologies that can achieve sufficient run times.

Cost estimates in general for plasma technologies cover a broad range from \$50 to \$2,500 per ton, depending on capacity, technology, and type of waste. Usually, cost estimates at early stages of technology development tend to be highly inaccurate. The success of a technology will be determined not only by performance, but also by its cost. The waste remediation and treatment marketplace will ultimately determine the opportunity for plasma technology application.

Some specific cost estimates are as follows:

- MGC Plasma Ltd and Retech Inc cost \$1800 to \$2450/ton at a 12 ton/day capacity and \$760 to \$980/ton at 26 tons/day.
- Integrated Environmental Technologies (IET) costs \$90/ton at 100 tons/day, \$250/ton at 10 tons/day, and \$480 to \$600/ton at 2 tons per day.

IET's costs are acceptable for use at smaller scale waste producers. This process would allow on site destruction, so a site could be converted from a RCRA to a non-RCRA site.

IET achieves lower costs by using a combination of plasma and joule (resistance) heating, plus carbon electrodes. Carbon electrodes don't require water cooling like the conventional metal electrodes, providing greater reliability (longer run times and less maintenance on the electrodes)

and higher energy efficiency. For high hydrocarbon feeds, cogeneration or chemicals production are possibilities. This area provides business opportunities for electric utilities to partner with chemical companies in Trigenation (combined production of electricity, steam, and chemicals).

The commercial status of IET's technology is as follows: (1) 1/2 ton/day existing demo unit for testing, (2) 10 ton/day proof of scale up unit operational April 1999, and (3) 2 ton/day commercial on site unit shipped to the customer in May 1999. Commercial scale units will process 2 to 100 ton/day.

In addition, there are other competing technologies that should be considered, such as the Westinghouse technology.

2.3.4 Biofiltration

Biofiltration is the use of a packed column (like a packed distillation column) to contact wastewater counterflow with air in the presence of nutrients. It provides a very compact treating unit. However, it is subject to upsets and biofouling. This is a compact version of a trickling filter or fix film biotreater referred to in logic diagram Figure 1-3.

2.3.5 Other

The most common end-of-pipe technologies are summarized in Figures 1-1 through 1-4. While the information presented doesn't include electrotechnologies, utility companies may want to use this information to help their customers, to obtain the benefit of load retention.

3

OPPORTUNITIES FOR PROJECTS AT SPECIFIC SITES

3.1 Double Distillation Related to Butanol/Water Separation

A Texas chemical operation faces expensive double distillation and waste treatment problems related to a butanol/water separation. This problem could be handled using World Wide Water Systems, Inc.'s large diameter hollow fiber membrane, perhaps paralleling the modular system developed by MTR (successfully used at Perkin Elmer).

The chemical operation has a byproduct stream that can be from 30% to 80% butanol, plus companion alcohols that have carbon numbers from C_3 to C_{12} . Using pervaporation, two splits could be made with membranes in order to eliminate the two distillation steps currently employed. Alternatively, the scheme could be membrane treatment, followed by distillation.

Concept	Step	Process	Stream Content
Two Step Membrane	1	Membrane	$H_2O + C_5$ plus C_4 minus
	2	Membrane	C_4 C_3 minus
Membrane and Distillation	1	Membrane	$H_2 + C_5$ plus C_4 minus
	2	Distillation	C_4 Other

Distillation may run 800 Btu/lb (1.9 MJ); membranes could run 200 Btu/lb Energy evaluation will be a key part of the test.

3.2 International Chemical Company Wishes to Eliminate U.S. Deep Wells

A chemical company with many locations in the U.S. operates deep wells with trace organics in the effluent. Literally millions of gallons are being sent downhole. A selective membrane process could take out the organic matter (e.g. acrylonitrile) and allow the water to be reused and/or sent to aerobic treatment or treatment by plant life. Another approach would be partial electrolytic conversion to a biotreatable material. The company has a desire to eliminate deepwells as a disposal method via edict and company policy.

3.3 Separation of Organic Volatiles From Water

Tracking of chemicals can create a major cleanup problem. A certain chemical processor must address the separation of organic volatiles from water prior to clean up. The use of membranes offer an alternative in water clean up systems. This company operates a major facility where this problem exists and would be open to installing a test package.

3.4 Multi-U.S.-Sited Petroleum Refiner Has a Major Problem in Louisiana

This facility faces a major clean up of its stormwater drainage system and its collection ponds which are heavily laden with organic sludges in the presence of VOCs. Super critical water oxidation is being considered to handle the sludge ponds. This is a possible opportunity to promote freeze concentration technology.

3.5 Large Natural Gas Company Is Moving Into Water and Wastewater

Several of the projects in this company have potential. One project that may initiate is related to the treatment of nonhazardous waste at a chemical company's WWT ponds. Tests in an oil-water removal system are needed in lieu of centrifugation and filtering. Microwave emulsion breaking may be applicable.

3.6 Multi-U.S.-Sited Petroleum Refiner Has a Major Problem in Texas

This plant is experiencing a serious problem with respect to the treatment of river water used in the plant for cooling, process, and power purposes. The system to be tested at the facility is a combination of pretreatment plus membrane. The total system will be utilized to:

- Remove large particles
- Remove hardness
- Remove colloids
- Remove turbid particulates

Pretreatment will use a special flocculent from Filter Flow Technologies Corporation, Clear Lake, TX. Following treatment, further softening and cleanup will utilize a special spiral wound allulasic membrane cartridge built to avoid scaling.

The system will utilize high-energy efficient, low-pressure pumps to save on both capital cost and operating and maintenance costs. This same system has potential at two unrelated chemical sites.

3.7 Ethylene Glycol Tainted With Animal Fat

A company is currently sending thousands of gallons of ethylene glycol (tainted with animal fat) to boilers and industrial furnaces (BIFs). A low fouling direct osmosis membrane system based on separating these components by molecular size would give value-added and recycle potential to both the fat and glycol.

4

OPPORTUNITIES FOR ELECTRIC UTILITIES AND ENERGY SERVICE PROVIDERS

Generic business opportunities for utilities and energy service providers are summarized in this section.

1. Water pinch represents a key way of both helping customers and increasing the use of electrotechnologies. It is clear from published water management treatment technology selection logic that there is a bias towards traditional non-electric approaches. The power of water pinch is that it not only brings the utility companies into their customers' plants, but it also levels the playing field, since all viable technologies are usually examined in this approach.
2. Educating customers relative to the benefits of some specific electrotechnologies, through publications (such as this one) and workshops can remove some of the bias, as well as uncover specific situations where utility providers can be of assistance to their customers. Through water pinch studies, technology demonstrations at customer facilities, and as a provider of business services, utility companies can provide additional value to their customers.
3. For utilities that are interested, there is an opportunity to take over the operation of facilities' water management as a business by itself, or in conjunction with operating all utility services.
4. The following existing and emerging technologies look promising and should be considered for promotion (demo or other):
 - Vapor electric compression evaporation (480 kWh/1000 gal (3.8 m³)) which is currently a major key for achieving zero discharge.
 - Freeze Concentration (375 kWh/1000 gal (3.8 m³) recovered) which has a niche market fit for wastewater containing a mix of both hazardous volatile and hazardous non-volatile material requiring destruction.
 - Direct Osmosis Concentration (almost 360 kWh/1000 gal (3.8 m³) recovered) which should find smaller scale niche markets such as bio-sludge dewatering, due to its tolerance for high solids loads.
 - A combination of reverse osmosis (20 to 30 kWh/1000 gal (3.8 m³) feed) and electrodialysis (60 to 90 kWh/1000 gal feed) which should be able to compete with thermal evaporators for water recovery.
 - Microfiltration and ultrafiltration (4 to 8 kWh/1000 gal (3.8 m³)) which is used for various pretreatment and post treatment polishing steps.

- Advanced distillation which has a U.S. potential to reduce reboiler duties by about 0.5×10^{15} BTU/yr (5.3×10^{17} J/yr) and condenser cooling water duties by almost as much, with a side effect potential to reduce evaporation losses from cooling water towers by 0.5×10^{12} pounds per year (0.2×10^{17} kg).
5. One emerging technology is singled out due to its great promise. That is the electrolytic partial or complete oxidation of hydrocarbons (8.5 kWh/1000 gal (3.8 m³)) feed in one partial oxidation, see Chapter 2 for more details). This technology is versatile and can potentially solve a number of difficult problems. If there exists a difficult organic/inorganic mixture that can't be economically handled with other approaches, just "zap" away all of the hydrocarbons or change them to something that can be handled. If there is something in a stream that makes it not amenable to biotreatment, just "zap" it to something that can be biotreated. If hydrocarbons need to be removed to protect an evaporator from heat transfer fouling or a membrane system from hydrocarbon induced damage, just "zap" away the hydrocarbons to the PPB level.
 6. Seven specific slipstream test opportunities are discussed in Chapter 3.

5

CONCLUSIONS

While electrotechnologies in general have not been given a fair hearing in the environmental community, now is the time to start putting things right, since a number of factors beneficial to electric options are falling into place.

The emerging shift from end-of-pipe to incorporating water minimization into the overall water management picture is definitely favorable for electric options (illustrated by the move to electrically intense vacuum vapor compression evaporation as a key component of the zero discharge approach).

Also, the general increase in salt content of streams due to the increased use of recycle provides an opportunity for membrane processes such as reverse osmosis combined with electrodialysis to be considered for removal of salts, or an essentially forced complete jump to zero discharge, and the use of electrically intense vacuum vapor compression evaporation.

The process industries are looking more closely at their water management costs and operations. This provides opportunities for sophisticated electrotechnologies to help with difficult problems, such as some mixed organic/inorganic contaminated streams, and possibly some unusual “at source treatment or separation problems”, where unique characteristics of electrotechnologies, and their small footprint, will give them advantages over traditional methods.

Also, the amount of difficult hazardous wastes that will need to be processed should increase as companies start to discontinue the practice of deep welling.

In addition, advances in electrotechnologies, now should improve their chances. Membranes now have longer run times, and there are new technologies (such as electrolytic oxidation of organics) that can be used in conjunction with older technologies.

The bottom line of all of this is that utility customers are more frequently getting “between a rock and a hard place” in the water management of **difficult** problems. These difficult problems can get utilities in the door. Because electrotechnology options are more numerous and better than they have been in the past, companies are more likely to find them to be an economical solution.

Water Pinch can also help utilities get in the door, to achieve the above.

Utilities that choose to go into the business of performing water management for their power customers have an even surer approach to seeing to it that electrotechnologies get a fair hearing. At the same time, they can earn profits from the water management business.

6

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A

ABBREVIATIONS AND ACRONYMS

AICHE	American Institute of Chemical Engineers	gpm	gallons per minute
API	American Petroleum Institute	HAP	hazardous air pollutants
ASB	aerated stabilization basin	HON	hazardous organic NESHAP
BAT	best available technology economically achievable	HRMS	high-resolution dioxin/furan analysis (ppq)
BEJ	best engineering judgment	I&M	inspection and maintenance
BHP	brake horsepower	ICAP	inductively coupled argon plasma spectroscopy
Biox	biological oxidation	IAF	induced air flotation
BOD	biological oxygen demand	IX	ion exchange
BPT	best practicable control technology currently available	LRMS	low-resolution dioxin/furan analysis (ppb)
BTEX	benzene, toluene, ethylbenzene, xylenes	MACT	maximum achievable control technology
BTU	British thermal units	MEK	methyl ethyl ketone
CAA	Clean Air Act	mgd	million gallons per day
CLP	Contract Laboratory Program (US EPA)	NAPL	nonaqueous phase liquid
CMA	Chemical Manufacturer's Association	NDMA	Oxidation by-product of UDMH (unsymmetrical dimethylhydrazine) and a product of dimethylamine interacting with nitrite. NDMA can be found in wastewater of chemical plants at ppb levels.
COD	chemical oxygen demand	NESHAP	National Emission Standard for Hazardous Air Pollutants
CPAS	clean process advisory system	NPDES	National Pollutant Discharge Elimination System
CPI	chemical process industries; corrugated plate interceptors	O & M	operations and maintenance
CVAA	cold vapor atomic adsorption spectroscopy	OCC	old corrugated containers
CWA	Clean Water Act	ORP	oxidation-reduction potential
CWRT	Center for Waste Reduction Technologies	P&ID	pipng and instrumentation diagram
DAF	dissolved air flotation	PAH	polynuclear aromatic hydrocarbons
ED	electrodialysis	PCP	pentachlorophenol
EPA	Environmental Protection Agency	PFD	process flow diagram
EPCRA	Emergency Planning and Community Right to Know Act	POTW	publicly owned treatment works
EPRI	Electric Power Research Institute	ppb	part per billion (%g/L)
GAC	granular activated carbon	ppm	part per million (mg/L)
GEP	good engineering practice	psi	pounds per square inch
GC/MS	gas chromatography/mass spectrometry	PVC	polyvinyl chloride
GFAA	graphite furnace atomic adsorption spectroscopy	QA/QC	quality assurance/quality control
gpd	gallons per day		

Abbreviations and Acronyms

RDX	research development explosive	TDS	total dissolved solids
RO	reverse osmosis	TOC	total organic carbon
SARA	Superfund Amendment and Reauthorization Act	TOX	total halogenated organics
SIC	Standard Industry Classification	TRI	toxics release inventory
SOCMA	Synthetic Organic Chemical Manufacturer's Association	TSS	total suspended solids
SOCMI	Synthetic Organic Chemical Manufacturing Industry	VCE	vapor compression evaporation
SOW	statement of work	VOA	volatile organic analytes
SVOA	semi-volatile organic analytes	VOC	volatile organic compound
SVOC	semi-volatile organic compound	WRC	Water Resources Council
		WW	wastewater

B

SELECTED INTERNET INFORMATION

Pall Corp: Military Environmental Solutions - Oily Wastewater

<http://www.pall.com/applicat/military/applications/wastewater.html>



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Using Membrane Technology to Minimize Wastewater

Improvements in polymer chemistry and materials have increased membrane use in wastewater minimization efforts.

by Larry Lien

As we move into the new millennium, waste reduction from all types of manufacturing -- from chemical and food production to heavy industrial machining, plating and stamping operations -- will be a major focus of many CEOs, environmental engineers and waste treatment operators. The holy grail has been and will continue to be zero discharge. However, no matter what the scope of a company's wastewater abatement program, membrane technology is likely to play a major role in achieving the objectives.

Choosing a membrane

Membrane technology covers a broad spectrum of pore sizes and materials. Membrane categories include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Figure 1 provides information related to membrane categories, their pore sizes and commonly filtered materials.

MF membranes have pore sizes ranging from about 0.1 micron to 1 micron. These membranes are commonly used to remove suspended solids and bacteria from liquids and gases and can be manufactured from a myriad of materials. Typically, MF membranes are made of polymeric material -- for the most part asymmetric; a list of commonly used polymers includes Teflon (PTFE), polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), cellulose acetate, polysulfone, nylon and polycarbonate. In addition, non-polymeric submicron membranes manufactured from durable materials such as ceramics and metallics also are used for MF separations.

Another generally accepted membrane category, UF membranes, encompasses a pore size range of 0.003 micron to 0.1 micron. Like the MF membranes, these membranes typically are an asymmetric polymeric; however, the larger-pore-size UF membranes are designed to remove

<http://www.manufacturing.net/magazine/polleng/archives/1998/pol0501.98/05akc1f2.htm>

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colloidal materials and viruses from liquid streams. The largest single use of smaller-pore-size UF membranes is to remove from cheese whey soluble proteins with a molecular weight greater than 8000.

For the NF range of membranes, the description becomes less well defined. These membranes initially were manufactured from asymmetric cellulose acetate, but now are more typically made of a thin-film composite -- a polymeric base such as polysulfone with a thin film, typically 0.2-micron thick, crosslinked and on its surface.

NF membranes have pore sizes ranging from less than 0.001 micron to 0.003 micron, and they reject on two levels. First, non-charged soluble organics are rejected on size and shape -- the molecules are simply too big to pass through the pores. The second level of selectivity is for charged soluble salts that are much smaller than the membrane's pores. These salts are rejected because water is more soluble in the membrane than is a specific salt. The tighter NF membranes -- those with the smallest pore sizes -- are so selective they can fractionate, or separate, divalent (+2 charge) anions from monovalent (+1 charge) anions.

Because NF membranes reject on both a charged and a non-charged basis, their use has been increasing in specialized applications. In the dairy industry, for example, NF membranes are used to fractionate 6 percent lactose from a 6 percent sodium chloride solution. The lactose is concentrated and simultaneously purified by removing the sodium chloride with NF membranes. In addition, NF membranes often are used to fractionate on a purely ionic level by rejecting sodium sulfates and permeating sodium chloride -- that is, allowing it to pass through -- from a mixed salt brine solution.

RO membranes are typically asymmetric cellulose acetate or thin-film composite membranes, with the most common thin-film composite being a polyamide film bonded to a submicron-pore-size polysulfone base. RO membranes primarily are used to remove salt from brackish and seawater solutions, but because the pores of these membranes are so small (approximately 0.0005 micron), the membranes also are used within industry to concentrate a variety of substances -- from antifreeze to wine. Power requirements comprise the major cost of running any membrane system and are directly related to pressure needs. Recent dramatic improvements have been made in polymer chemistry and manufacturing, increasing RO membrane efficiency, lowering membrane operating pressures and reducing costs. These improvements have significantly expanded the use of membrane technology for water treatment.

A prime candidate

Equally important to the selection of the proper membrane is the platform of membrane configuration. All the membrane categories discussed earlier can be configured as tubular, hollow-fine fiber, flat sheet in a plate-and-frame or spiral-wound (for increased surface area) systems. As mentioned previously, improvements in polymer chemistry and materials have expanded the boundaries in which membranes operate. MF, UF, NF and RO membrane systems are functioning in applications across the pH spectrum -- from 0 to 14 -- on strong industrial solvents, at temperatures of more than 100°C and at pressures up to 2000 psi and higher for some

plate-and-frame systems.

The variety of membrane types and platforms to configure them makes membrane technology a prime candidate for wastewater abatement and resource recovery. However, wastewater is variable in nature and volume, so efforts using membrane technology to resolve wastewater problems must be carefully bench-, pilot- and field-tested to ensure the success of the scale-up systems.

Many successful membrane applications can be seen in the metal plating industry. For example, a copper rod mill produced a copper- and acid-laden rinse stream that had been sent to a conventional precipitation system. A severe water shortage, as well as problems associated with sewerage of the water from the filter press because it contained 2 parts per million (ppm) to 3 ppm residual copper, forced the mill to look at membrane technology. By using an acid-stable, RO thin-film-composite spiral-wound membrane system, the mill was able to concentrate copper sulfate and sulfuric acid from the copper rinsing operation at a pH of 1.5. After going through a two-pass RO system, the permeate was clean enough to be reused as rinse water. Furthermore, by following the RO system with an NF spiral-wound system, the copper was fractionated from the acid and recovered, while the purified acid was reused as part of the makeup for a pickling bath. Although the system design was elaborate, it paid for itself in just over one year. Figure 2 shows the system's configuration.

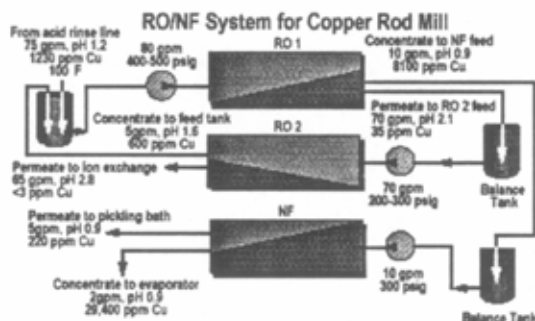


Figure 2. An RO/NF membrane system allowed a copper rod mill to concentrate copper sulfate and sulfuric acid from a copper rinsing operation and reuse the permeate as rinse water.

The chemical processing industry has used membrane technology in a similar manner to recover valuable organic material from chemical processes. Using seawater-type RO membranes, a chemical processing company was able to recover residual soluble organic material from a wastewater stream. The wastewater contained polymer -- propylene glycol, molecular weight 72 -- which was present in low concentrations from a rinsing operation. The RO membrane system first concentrated the glycol from 1 percent to 10 percent. Using an NF membrane system, the 10 percent glycol was then purified by permeating the propylene glycol, as well as by removing unwanted residual divalent salts and other organic materials with molecular weights greater than 200. This two-step

membrane approach converted a toxic waste stream into a valuable product. Furthermore, the RO permeate water can be reused in the plant as boiler-feed makeup water or as cooling tower water. The payback on such equipment was less than one year. The RO-NF system configuration is shown in Figure 3.

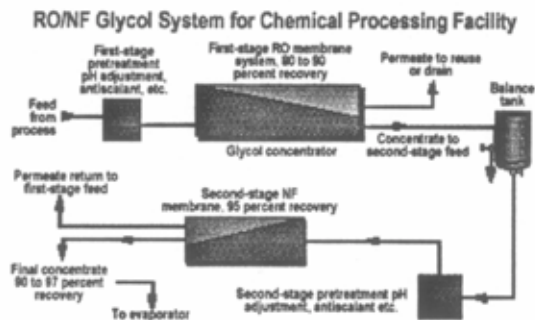


Figure 3. Using seawater-type RO membranes and an NF membrane system, a chemical processing company converted a toxic waste stream into a valuable product.

Another company -- a bottle washing facility -- also used spiral-wound membrane types to reclaim hot, 50°C caustic cleaning solutions with a pH of 13.5. The first-pass system used a high-pH-stable UF membrane system to remove suspended solids and colloidal solids from the caustic solution. The UF permeate then was further purified using an RO membrane that removes virtually all soluble organics and some salts, and permeates a purified caustic solution reused on the bottle washing lines. Despite the fact that caustic is relatively cheap to purchase, disposing of it can be costly because of its organics and the salts created by neutralization. Therefore, reclamation of hot caustic using membrane-based systems is quite cost-effective if one totals the savings associated with recovered caustic, the heat recovered and the volume of waste reduced. Figure 4 shows the UF/RO system configuration used for the bottle washing facility.



Figure 4. A bottle washing facility used spiral-wound membrane types to reclaim hot caustic cleaning solutions.

Clearly, the most appropriate application for membrane technology in relation to wastewater is to recover and concentrate -- or purify -- something of value, such as a metal or a soluble organic. If one can creatively develop a process to accomplish this task, then the wastewater can be converted from the proverbial "sow's ear into a silk purse."

Larry Lien is director of Applications and Process Development with Osmonics Desal, Escondido, Calif., 760-735-6210.

Regulatory Impact

- General requirements under 40 Code of Federal Regulations (CFR), Part 122, which details the National Pollutant Discharge Elimination System (NPDES)

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Magazine Articles

Industrial Wastewater: No Room for Afterthoughts

Minimizing waste generation begins with looking at the wastewater treatment process as a whole, not as an afterthought.

Cathryn Owano Hodson, Associate Editor

The world of water and wastewater management as we know it is changing. Publicly-owned water treatment plants can now be owned and operated by private corporations, a move that will change how POTWs are legislated and regulated, but not their purpose.

Treating and controlling industrial wastewater is no different: the methodology may change or evolve, but the purpose remains the same. For years industry has been finding ways to comply with local, state and federal wastewater regulations to reduce effluent contaminants. As these standards become increasingly more strict, industry continues to find ways to lower contaminant levels by designing processes that reduce contaminant generation throughout the process.

"Your environmental engineer isn't coming in and saying, 'You need to go back and look at [the process],'" says Bill Ross, senior office manager for Lockwood Greene Technologies in Atlanta. "It's fine-tuned to the point where the people actually designing the process are finding ways to minimize waste generation as part of the initial process design and not as an afterthought. They're asking, 'How can I reuse this stream, [or change the process conditions] to minimize waste generation?'"

The issues

When a new technology becomes available, very often its first costs are prohibitive. But as volume increases and more efficient manufacturing techniques are found, prices come down and the technology becomes more readily available. Yet there are other reasons for innovation than money. Increased knowledge of the environment and its requirements, as well as better measurement techniques, also lead to new technology and equipment.

In the past, removing VOCs from the influent typically meant air stripping. "EPA has started taking a stance on 'what good does it do to

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8/17/99

clean up the water and pollute the air?" and vice versa," says Lockwood Greene's Ross. "What you're starting to see is the wastewater permit application asking about solid waste -- 'what do you do with it? Do you have hazardous waste? What do you do with it?' They're not asking for amounts or anything, but it's become key that when you answer yes to some of these, they start coordinating with other departments to make sure you're not just transferring the problem from one area to another."

How much is too much?

Concerns by anti-regulatory sentimentalists and industrial lobbyists that the Environmental Protection Agency has too much regulatory power have spurred current reform cries. Some say federal regulations need to be based more on scientific data and research, to be more realistic and site specific. Still others feel that stiff regulations and enforcement are needed, necessary and increasingly important. How much contamination is too much? When can it be left alone or untreated? As technology advances and contamination can be detected at lower and lower levels, will regulations continue to drop restrictive limits ad infinitum?

"I think it will depend on public health studies supporting the need to remove below certain levels," says Wayne Roberts, environmental project engineer at Lockwood Greene in Atlanta. "Certain thresholds, based on scientific study, have been established to protect human health. I think that when they are able to do studies to show the effects of low contamination levels, then there will be some reasons to lower those levels or those standards."

"Or not to lower them, as the case may be," adds Lockwood Greene's Ross. "Sometimes when you're talking about very sensitive items, such as pesticides, from a public viewpoint--if you can measure it, it's too much. Even though that may not be factually correct."

As detection technology improves to the point of being able to identify quantities down to the parts-per-trillion level, "We have to ask ourselves, 'How clean is clean?'" acknowledges Nathan Redwine, PE, director of business development at Diversey Water Technologies Inc., Chagrin Falls, Ohio. "In some cases, the discharge limits are lower than the level of contaminants in the incoming supply water."

Aquatic life concerns

Other considerations for contaminant levels include aquatic life toxicity. Early EPA goals, according to Paul Sinisgalli, associate, Camp Dresser & McKee, Boston, were to make U.S. waterways swimmable and fishable. Part of EPA's regulatory objectives is to ensure that aquatic life, in some ways more sensitive to toxic substances than humans, survives to continue and complete the food chain.

What about fish who are exposed to known toxins via wastewater discharged to a river? There is the possibility that cooking these fish does not eradicate the toxins. In such a case, are risk assessments being extrapolated?

"That's where I think the science, as currently applied, may be weak,"

Camp Dresser & McKee's Sinisgalli says. "Many times there's an assumption that somebody's out there every day fishing and they're cooking the fish and eating fish X number of times a year, which may or may not be valid. It certainly is invalid for the whole population of a particular region. Many risk assessments conducted to establish effluent toxicity limits make a number of assumptions and simplifications that are probably on the conservative side. There are a lot of factors that are not considered which affect the bioavailability of contaminants such as river chemistry, sedimentation and natural degradation."

The technologies

Answering these concerns is not easy. While Congress struggles with just how much regulation and enforcement power the EPA should be blessed with, engineers and manufacturers struggle with how to battle the continuing challenge of wastewater contamination. The degree of wastewater treatment required, because of the strict effluent contamination level limits, has increased, which has in turn driven up treatment costs.

"It only makes sense at some point to be recycling your wastewater," says CD&M's Sinisgalli. "In the Boston area, where water has become more and more expensive, due to the high costs of treatment through the local sewer authority, industry is evaluating recycling more frequently: to save on the purchase cost of their water and to avoid having to pay a hefty fee to treat the sewage once discharged to the local sewer."

Wastewater treatment processes can be divided into three broad types: biological, chemical and physical.

"Biological treatment uses microorganisms to consume organics," explains Sinisgalli. "Physical processes sometimes precede biological treatment. It may consist of taking the wastewater, placing it into a [clarifier] tank and allowing settling to occur. The third type would be chemical treatment, which is usually a combination of physical and chemical. For example, the addition of chemicals to a solution containing metals--the metals react with the chemicals, form a precipitate and are removed by settling."

Membrane technology, a physical treatment, separates contaminants from wastewater by molecular weight and size. A growing field in the wastewater treatment industry, membranes hold a lot of promise as an evolving technology. Four basic membrane methods accomplish contaminant separation from water: microfiltration, ultrafiltration, nanofiltration and reverse osmosis. (See *Pollution Engineering*, July 1995, for more complete coverage of membrane technology).

Microfiltration is the most porous cross-flow filtration method, handling particles from 0.01 microns to 5 microns and operating under 20 to 100 pounds per square inch (psi) pressures.

Ultrafiltration "removes colloidal particulate, a particulate so fine that it basically would not separate by gravity," says Lockwood Greene's Charlie Nichols, manager of water and wastewater services. "It's also able to remove very large molecular weight dissolved-organic materials, depending on how fine the ultrafilter membrane is." Ultrafiltration pore sizes range from a few molecular diameters to about 0.01 microns.

Nanofiltration works in the 150 to 300 psi range and can remove some inorganic ions. "It would actually remove calcium and magnesium to a certain extent due to a partial softening in a water stream," says Nichols.

Reverse osmosis operates under high pressures, in the 200 to 1200 psi range, and can remove low-molecular-weight organic materials and salts while allowing water and solvents to pass. It is used primarily in desalination applications, although it also is used in industrial applications for separating chemical and metallic salts.

Conclusion

Controlling and treating wastewater continues to evolve and will provide enough challenge to engineers, manufacturers and legislators for some time to come. Increased restrictions on effluent levels are challenging everyone to find ways to reduce waste from the very start of the design process. Paul Sinisgalli counsels that it's important to remember each industrial wastewater stream is a little bit different and that there is "a tremendous variety from industry type to industry type."

"Know what you're starting with and know what you've got to produce," adds Charlie Nichols. "A lot of communication is needed between the engineer and the owner to get the proper information and get it in the proper format. And that same communication has to be done with the regulatory agencies too."

Non-Point Source Pollution: Design Concerns

Non-point source pollution can be a contaminant that is spilled or that runs off from something else, such as a pesticide, chemical or compound washed into the soil or groundwater through rainwater seeping into the ground. Non-point source pollution also can emanate from something that is buried, and can affect regulated direct dischargers.

"When regulatory agencies now set water quality standards for surface water or river basins," says Camp Dresser & McKee's Paul Sinisgalli, "waste load allocations are established by taking into account all the different point sources and non-point sources. Accounting for all the non-point sources will impact everybody's pollutant loads, whether it's a storm sewer, a public wastewater treatment plant or an industrial wastewater treatment plant."

"One of the biggest challenges left in water pollution control in the state of Georgia is runoff from construction industries--soil sediment," says Bill Ross, office manager at Lockwood Greene Technologies in Atlanta. "Not what you'd ordinarily think of as pollutants. And it can be a real problem...when new construction goes on and you have a beautiful lake...that all of a sudden turns brown."

Some believe non-point source pollution, or the treatment of runoff, is a tougher problem than treating process wastewater, due to the variability of flow. "One design criteria agencies are beginning to impose is the capture and treatment of a 20-year return storm," says Charlie Nichols, manager of water and wastewater services at Lockwood Greene. "This could amount

to two million gallons of runoff on an industrial site over a one-day period compared to the typical storm event of 50,000 gallons. To design a capture, pumping, storage and treatment system for such extremes of flow rate requires careful thought and planning."

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IDEA BANK

Wastewater Treatment System Employs Innovative Separation Process

by Kathie Canning, Associate Editor

The USBF treatment system uses upflow sludge blanket filtration in a prism clarifier to create a high rate of separation in organics-contaminated wastewater streams. After microbial cells and water enter the bottom of the clarifier, they begin to rise. Upward velocity decreases until the flocculated cells become stationary, forming filtering media that separate out colloid and very fine particles. To enhance the filtration process and increase the number of microbial cells searching for "food," the process is operated at a high sludge concentration. The "superactivated" biomass then feeds on a wider range of organic materials, including some previously considered non-biodegradable. Aeration, nitrification, denitrification, clarification and sludge stabilization are accomplished inside one compact reactor, substantially reducing the system's footprint.

Purestream/Ecofluid, Walton, Ky. Walton, Ky.

Process Employs Electrocoagulation for Low-Cost Wastewater Recycling

An electrocoagulation- and filtration-based system allows complete recovery of all organics- or metals-contaminated wastewater. A two-step procedure reduces rinse water volumes and returns the water to the process or provides additional rinses to achieve "exponential" dilution of the carryover, reducing water rinsing volumes by 90 percent to 95 percent. Those rinse waters not returned to the process are treated in the Water Management System, which removes solids through clarification and filtration without the use of chemicals. The clarified water then passes through an ionic, electrocoagulation-based polishing filter that virtually eliminates water impurities. Oxygen used in the process lowers the surface tension of the water, often resulting in the returned water being of a better quality for rinsing than the original water used. Ideal for metal platers, the system reduces water requirements and sludge and provides excellent chemical/metal recovery.

PASCO, Hillsboro, N.C.

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Industrial Pure Water

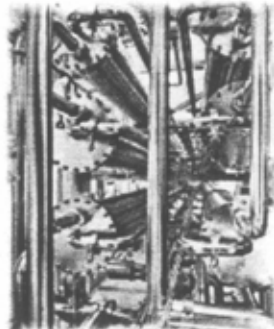
ZENON is the technology leader in designing, fabricating and installing High Purity Water Systems for health sciences and general industry. ZENON's introduction of Hot Water Sanitizable membrane based technology to the pharmaceutical industry is still being hailed as "the breakthrough technology everyone has been looking for".

ZENON's introduction of High Resistivity Reverse Osmosis Technology, which produces water that exceeds new USP XXIII Purified Water Standards, eliminates the need for post reverse osmosis treatment which can recontaminate product water.

These breakthroughs, and ZENON's extensive validation and turn-key experience, have pharmaceutical and biotechnology customers celebrating ZENON as the technology leader capable of customizing leading technology to meet their needs and exceed their pure water quality requirements.

Hot Water Sanitizable Double Pass RO and the first High Resistivity RO to meet new USP XXIII Purified Water Standards - two important industry firsts from ZENON to meet industry's pure water requirements well into the future.

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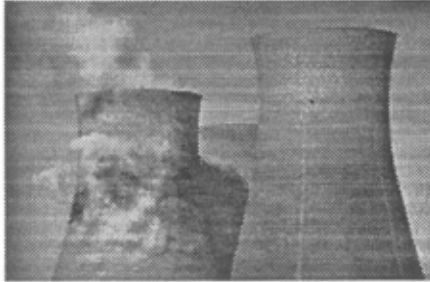


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Industrial Processing and Power



The more things change, the more they stay the same. Industrial fluid processing is always looking at ways to do the same things, take care of the bottom line. The technology that Osmonics offers in industrial separations and water purification allow the bottom line to be cleaned up literally, by producing less waste, by offering ways to recover material that would have been discarded as waste, and by offering better ways to treat product that is waste.

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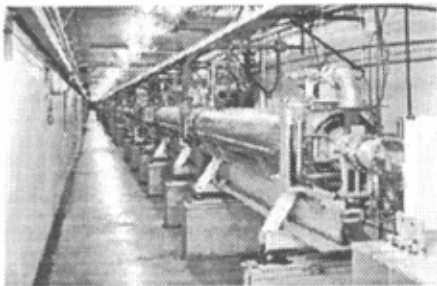
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Piping Sanitization



Processing plants in the beverage, semiconductor and pharmaceutical arenas have to deal with the storage and distribution of process fluids. Every system requires careful attention to periodic cleaning and sanitizing of installed tank and piping systems. With increased regulatory issues and competitive pressures, many companies are replacing or supplementing standard chemical sanitizing with on-site ozone.

At Osmonics®, we understand the need to effectively maintain a clean process environment for ultimate product quality. On-site ozone generators provide one of the most powerful oxidants available for sanitization of installed piping systems. Ozone is preferred in many applications due to on-site generation, short half-life and high oxidation potential. Because the final by-product is simple oxygen, rinsing and disposal issues are nonexistent.

Osmonics offers the most complete ozone sanitization systems available with in-line fluid monitors, ambient gas monitors, PLC/computer control, automatic injection and catalytic destruct units. All of this allows Osmonics to provide the right equipment to meet almost any sanitization requirement.

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Separation and Recovery of Valuable Materials From Process Streams



In many different chemical manufacturing facilities, one of the most important issues is the purity of the raw materials. Chemicals are manufactured and need to be diluted before they can be sold. The most frequent diluent is water. Since the chemicals need to be the purest possible, the water that is diluting the chemical must also be of the highest purity. Reverse osmosis and de-ionization allow water to reach the ultrapure state that removes even the smallest of impurities.

Osmonics has been manufacturing ultrapure water systems for years, and has experience designing, manufacturing, and installing them. In many cases, there are special requirements due to the locations that the equipment will be installed. In other cases, the equipment must be able to be controlled from a central control center. Osmonics has experience with a variety of controllers and can design and build a system to meet the needs of each individual application.

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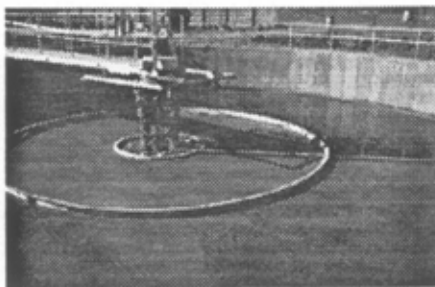
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Water Purification



Water purification plays an important role in many industries. Some of these include beverage bottlers, pharmaceutical companies, power generation, electronics manufacturing, and municipalities. The level of water purification required within these industries can range from microorganism and TDS removal for the beverage and municipal markets to USP and 18 Megohm quality water for the pharmaceutical and electronic markets.

Proper equipment selection is required to achieve proper water purification. This equipment may include media filtration, water softening, carbon filtration, reverse osmosis, deionization, ozonation, and distillation. Equipment arrangement is also an important factor for ensuring proper water purification, especially when membrane systems are involved. Proper pretreatment will significantly improve membrane element life and performance.

At Osmonics[®] we design and manufacture all of the necessary water treatment equipment to meet your water purification objectives. This sole source capability allows us to provide our customers with sound engineered solutions for their particular water purification objectives. In addition we manufacture the necessary depth filters, pleated filters and membrane elements for membrane equipment.

Osmonics can custom engineer equipment to meet our customers requirements. This may include special instrumentation, controls, and material requirements. We also offer a line of pre-engineered equipment which is a fast economical solution for many applications. All of our custom and pre-engineered systems are quality pre-tested at the factory to ensure proper operation in the field.

Osmonics has been working with customers for over 25 years to ensure proper equipment design and layout. Let us provide a solution for you.

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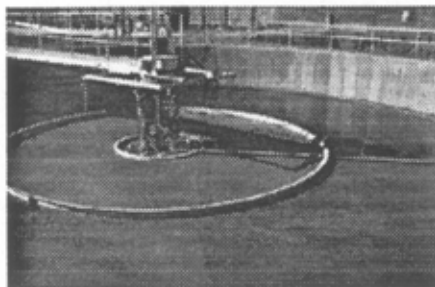
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Wastewater Color Removal



The environmental compliance requirements become increasingly more difficult to attain in both wastewater discharge and chemical handling. In addition, the costs of traditional treatment methods, off-site waste treatment, and discharge permits are rising tremendously.

Osmonics offers ozone as an alternative to traditional color removal methods. Ozone treatment offers dramatic benefits that are well contained and "hands-off," reducing the cost of operation while providing a very strong oxidant. Osmonics and Fuji have formed a team, and can now offer a line of medium frequency ozone generators that can provide high concentrations of ozone for the large oxidation requirements for the pulp and paper industry. Osmonics'® new ozonators can provide up to 15 wt. % concentration of ozone with lower electrical requirements, making the capital investment economically justifiable.

Osmonics ozone equipment also benefits waste treatment processes by drastically reducing discharge levels of color, odor, and taste. Ozone treatment is much more efficient than traditional oxidation treatment methods. For extremely high oxidation needs such as TOC reduction, ozone is often effective in conjunction with traditional oxidation chemicals in a hyperoxidation process.

In addition to ozone, Osmonics is the leader in new membrane technology being used to reduce color, TOC, and BOD as a result of waste processes. Osmonics' systems can provide UF systems for removal of color constituents and TOC, or NF systems for more strict requirements. For the most stringent requirements, RO can be used to reduce waste or reuse water. With Osmonics working on your side, almost any problem has a solution to fit your needs.

Micro-Gap is a trademark of Fuji Electric, Ltd.

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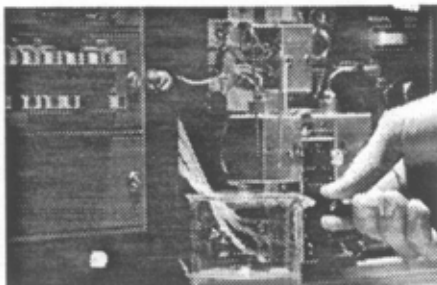
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Chemical Synthesis



In many different chemical manufacturing facilities, one of the most important issues is the purity of the raw materials. Chemicals are manufactured and need to be diluted before they can be sold. The most frequent diluent is water. Since the chemicals need to be the purest possible, the water that is diluting the chemical must also be of the highest purity. Reverse osmosis and de-ionization allow water to reach the ultrapure state that removes even the smallest of impurities.

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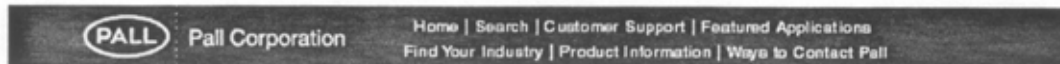
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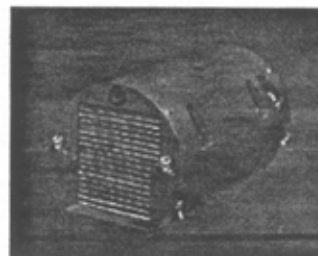
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Membrane Solutions for Water Treatment: Benefits of Membrane Technology...Think Pall

Pall is a leading supplier of microfilters, ultrafilters, nanofilters and reverse osmosis (RO) membrane filtration systems for processing water in both the municipal and industrial markets. Several important factors have contributed to the rapid acceptance of these systems:

- Membranes trap impurities by means of a porous barrier that is fixed in place; impurities are simply too large to pass through.
- Membranes remove these contaminants by controlling the pore size. If there are rapid changes in the feedwater composition, leakage of contaminants through the membrane will not occur.
- Membranes eliminate the need for the continual addition of chemicals, as is necessary in other separation systems. Chemicals are introduced to agglomerate or adsorb impurities which increases the effective size of contaminants so removal is achieved.
- The ability to separate contaminants from water is independent of the number of solids in the feedwater. Systems that rely on chemical addition must be adjusted continuously to compensate for changes in water composition. This makes them more costly and more complex to operate.
- Membrane systems are capable of processing high feedwater flows.
- Pall Water Treatment Systems are designed to occupy a smaller overall footprint when installed. The compact design and long service life of the filter modules make them an ideal system for any water application.
- When compared to conventional systems, membrane technology significantly reduces capital and operating costs.
- Most important of all, Pall is committed to utilizing only the highest quality components, materials and design methods. This ensures the end user round-the-clock reliability and high quality product-water.




Pall Rochem Nanofilter Module




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Chemicals and Polymers

Chemical and polymer production facilities combat fierce global competition by continually reducing their manufacturing costs and by maximizing their production efficiencies. By deploying Pall Corporation's family of filtration and separation products, chemical and polymer producers gain a competitive edge.

It's no secret that the diverse end-users of these products -- including producers of electronics, pharmaceuticals, polymer films and fibers -- pass on their stringent cleanliness and purity requirements. This makes filtration and separation more important than ever. It not only helps improve efficiency and yields, but protects expensive equipment from fouling, erosion and corrosion, which can lead to costly repairs and downtime.

Following are three major chemical/polymer industry applications for which Pall specifies filters:

- Catalyst Protection/Recovery
- Equipment Protection
- Finished Product

Catalyst Protection/Recovery

Catalyst life and costs are critical to many chemical production processes. This makes catalyst protection and recovery a major opportunity -- and challenge -- for Pall Corporation. Pall offers a wide range of products to remove both solid and liquid contaminants from the various feed streams entering the reactor process.

Pall's product menu includes disposable or metallic filters for applications in which solid loading rates are fairly low, and backwash or blowback filters for applications in which solid loading rates are higher. For example:

Pall Ultipor GF Plus®, Profile®, Ultipleat™ Profile® and HDC II® filters are well suited for secondary and tertiary catalyst recovery, water filtration, and for the removal of contaminants that are present prior to entering the reactor. These products serve as final product filters as well, helping to ensure product quality.

For primary catalyst protection or recovery, regenerable blowback or backwash filters are recommended. These systems operate in a fully automated mode, thus reducing labor and equipment downtime.

Pall PhaseSep™ Liquid/Liquid Coalescers are widely used for removal of dispersed, free liquid catalyst from reaction products.

Equipment Protection

Pall Seprazol Liquid/Gas Coalescers remove liquid aerosols from gas

streams thereby reducing the maintenance requirements of reciprocating compressors, fuel gas burner nozzles, gas separation membranes, and absorbent beds.

Pall PhaseSep™ Liquid/Liquid Coalescers remove organics from wastewaters thereby minimizing the fouling of packed or trayed towers.

The purification of plant makeup water with a Pall Microza hollow fiber microfiltration system prolongs the life and reduces the cleaning frequency of reverse osmosis membrane systems.

Pall pleated, polymeric Septra backwashable filters remove contaminants from the feedstocks fed to electrochemical cells, thereby extending the life of the ion exchange membranes.

Final Product Filtration

• Chemicals

Fine filtration is often required to ensure high product quality at the final chemical processing stage. This process removes particles and other process contaminants such as rust and water, along with byproducts of the reaction and environmental contaminants.

For these applications, Pall liquid/liquid coalescers are recommended for the separation of liquids, and Pall's disposable and metallic media to remove other contaminants, in order to meet stringent product cleanliness requirements.

• Polymers

Fine filtration is a necessity at the final polymer processing stage in order to ensure optically clear and strong fibers, films or resins. The final melt filter provides a "last chance" to remove oversized and unwanted particles and gels that interfere with the desired product quality.

Pall melt filters – such as Segmet®, Segmax® and PMF® – are instrumental in maximizing product quality and product yields, as well as achieving uninterrupted melt filter runs.

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Target:

Chemicals, Petroleum and Natural Gas

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